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DEVELOPMENT OF A SULPHUR TRIOXIDE DETECTOR*

This report was prepared as part of a project funded by the Environment Canada, by the Hydro-Quebec Research Institute. It deals with the progress of the research that led to the development of a laboratory prototype SO_2 detector. The prototype is based on the principle of gas permeation cells. The detection element of the gauge is composed of a K_2SO_4 membrane, a platinum electrode in the reference compartment and a gold electrode in the detection compartment. The test gas is the reactant gas. The gauge detects sulphur dioxide with good selectivity in the presence of various thermal power stations.

by

A.M. Chamberland and André Bélanger

Report APCD 79-1
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ABSTRACT

This study was undertaken on behalf of the Environmental Protection Service, Environment Canada, by the Hydro-Quebec Research Institute. It deals with the different stages of the research that led to the development of a laboratory prototype SO_3 -specific gauge. The prototype is based on the principle of gas concentration cells. The detection element of the gauge is composed of a K_2SO_4 pellet, a platinum electrode in the reference compartment and a gold electrode in the detection compartment. The tests given in this report show that the gauge functions adequately with gases similar to the gaseous emissions from thermal power stations.

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RÉSUMÉ

Le présent rapport a été rédigé pour le compte du Service de la protection de l'environnement du ministère de l'Environnement du Canada par l'Institut de recherche de l'Hydro-Québec. Il relate les étapes de recherches qui ont conduit à la mise au point d'un prototype de laboratoire d'une jauge spécifique au trioxyde de soufre. Le prototype mis au point fonctionne suivant le principe des piles de concentration gazeuse. L'élément de détection de cette jauge est constitué d'une pastille de K_2SO_4 , d'une électrode en platine dans le compartiment de référence et d'une électrode en or dans celui de détection. Les essais présentés dans ce rapport démontrent que cette jauge fonctionne adéquatement en présence de gaz similaires à ceux des effluents gazeux des centrales thermiques.

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1.2 SO₂ Measurement Project

It is well known that gaseous emissions, with a high sulfur content, can have up to 50 ppm by volume of SO₂, which is largely responsible for the corrosive effects of these emissions. Following discussions with representatives from Environment Canada, it was agreed that the research would concentrate on the specific measurement of SO₂ in the presence of other pollutants and at concentrations similar to those found in emissions from thermal power stations fueled by heavy oil or coal.

This report first describes the development of a laboratory prototype of a specific SO₂ detector, and then details its performance.

1 INTRODUCTION

1.1 Previous Work

A group of researchers at the Institut de recherche de l'Hydro-Quebec (IREQ) has been working for the last few years on a research project to develop solid electrolyte detectors for gaseous pollutants (1-4). The experimental findings have demonstrated that such sensors can adequately detect gaseous sulphur compounds, carbon oxides and light hydrocarbons, and nitrogen oxides. Other tests have extended the application of this same detection principle to the measurement of toxic gases such as arsine, phosphine and some metal hydrides. IREQ holds patents on all these detectors in a number of countries: Canada, the United States, England, France, Germany and Japan (5).

During the first phase of the project, special attention was devoted to total sulphur detectors. Development of laboratory prototypes was followed by the development of an industrial prototype for the continuous measurement of total sulphur in gaseous emissions.

1.2 SO₃ Measurement Project

It is well known that gaseous emissions with a high sulphur oxides content may have up to 300 ppm by volume of SO₃, which is largely responsible for the corrosive effect of these emissions. Following discussions with representatives from Environment Canada, it was agreed that the research would concentrate on the specific measurement of SO₃ in the presence of other pollutants and at concentrations similar to those found in emissions from thermal power stations fuelled by heavy oil or coal.

This report first describes the development of a laboratory prototype of a specific SO₃ detector, and then details its performance.

2 THEORY

2.1 Basic Principle

The determination of gaseous oxides by potentiometric measurements is based on the use of a concentration cell. As shown in Figure 1, the sensing element can be in the form of a pellet, and should contain the oxyanion (sulphate) of the anhydride (SO_3) to be detected. The solid electrolyte selected for the pellet should allow the desired electrochemical equilibrium to be attained and, under the operating conditions of the detector, should have adequate ionic conductivity. For the tests described in this report, potassium sulphate was selected as the solid electrolyte. It has good conductivity above 580°C and does not corrode the platinum electrode, as was observed in experiments with lithium sulphate. The concentration cell may be represented by:



where the partial pressures on the two sides of the electrolyte are different.

The electrochemical reaction is given by:



The electromotive force (emf) of this concentration cell is defined as:

$$E = \frac{RT}{2F} \ln \frac{P_{\text{SO}_3} (P_{\text{O}_2})^{1/2}}{P'_{\text{SO}_3} (P'_{\text{O}_2})^{1/2}} \quad (3)$$

where:

E	=	emf
R	=	gas constant
T	=	temperature, $^\circ\text{K}$
F	=	Faraday number

According to Equation 3, the emf of such a detector depends on variations in the partial pressure of both SO_3 (P_{SO_3}) and O_2 (P_{O_2}) in the two chambers.

In the course of previous studies (1), the circulating gas reference chamber was first replaced by a solid electrode reference system of the Ag/Ag^+ type, then by a $\text{ZrO}_2 (\text{O}^{2-})/\text{O}_2$ system, and then by a chamber in which P_{SO_2} and P_{O_2} are held constant by thermal decomposition of a sulphate. From both a thermodynamic and practical point of view, the latter proved more reliable and hence was used for the specific SO_3 detector project.

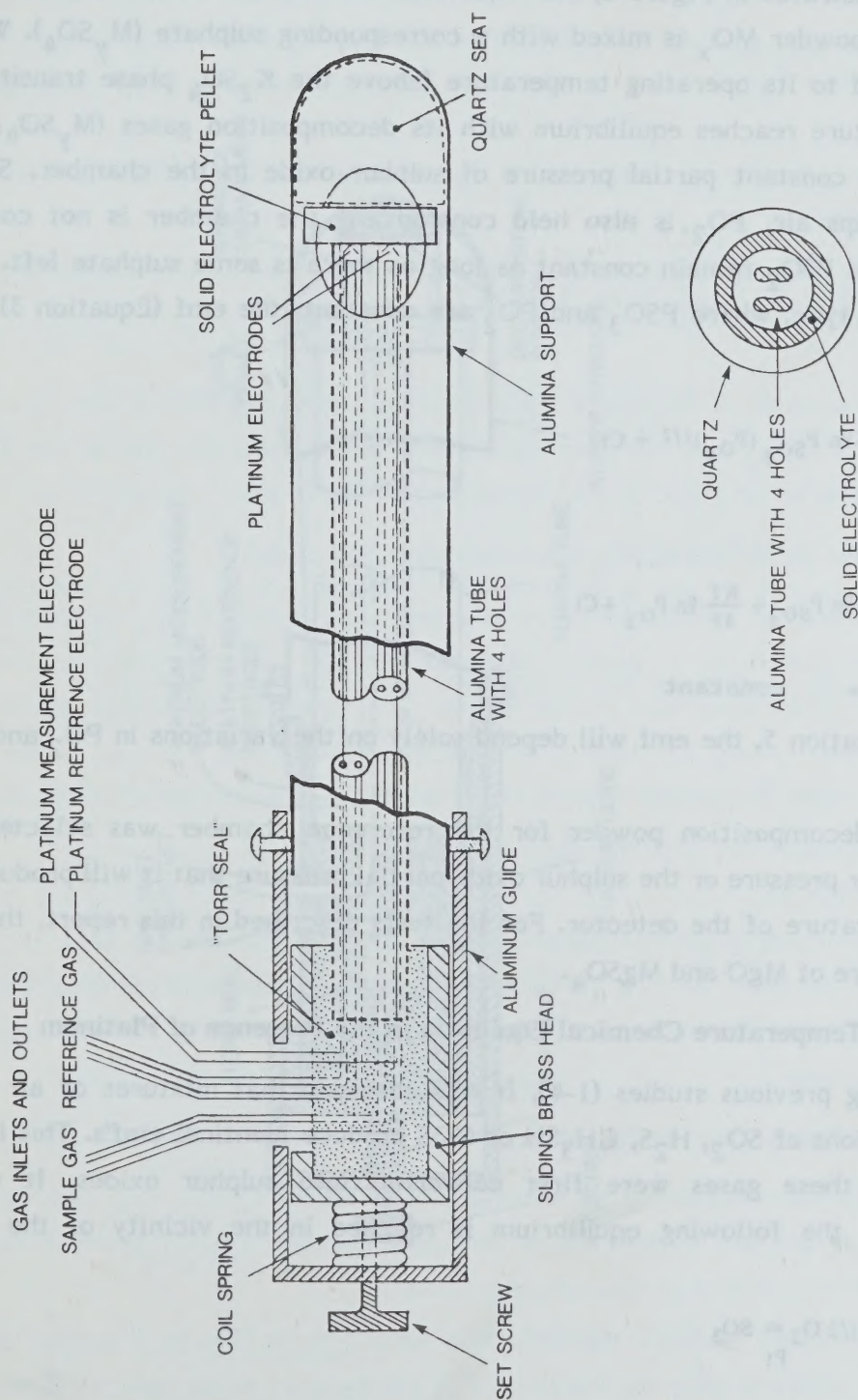


FIGURE 1 DESIGN OF A DETECTOR WITH A CIRCULATING-GAS REFERENCE CHAMBER ON THE SAME SIDE OF THE ELECTROLYTE AS THE SAMPLE CHAMBER

As illustrated in Figure 2, the reference chamber is a sealed crucible in which a metallic oxide powder MO_x is mixed with a corresponding sulphate (M_ySO_4). When the detector is raised to its operating temperature (above the K_2SO_4 phase transition), the MO_x/M_ySO_4 mixture reaches equilibrium with its decomposition gases ($M_ySO_4 \rightleftharpoons MO_x + SO_2$), creating a constant partial pressure of sulphur oxide in the chamber. Since the chamber also traps air, PO_2 is also held constant. If the chamber is not completely gastight, PO_2 and PSO_2 remain constant as long as there is some sulphate left. With an apparatus of this type, where PSO_3 and PO_2 are constant, the emf (Equation 3) is given by:

$$E = \frac{RT}{2F} \ln PSO_3 (PO_2)^{1/2} + Ct \quad (4)$$

or

$$E = \frac{RT}{2F} \ln PSO_3 + \frac{RT}{4F} \ln PO_2 + Ct \quad (5)$$

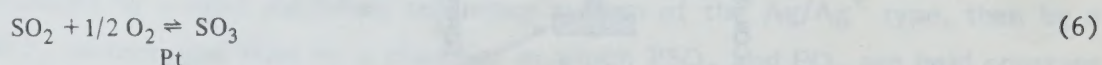
where: $Ct = \text{constant}$

According to Equation 5, the emf will depend solely on the variations in PO_2 and PSO_3 in the sample.

The decomposition powder for the reference chamber was selected on the basis of its vapour pressure or the sulphur oxide partial pressure that it will produce at the operating temperature of the detector. For the tests described in this report, the powder used was a mixture of MgO and $MgSO_4$.

2.2 High Temperature Chemical Equilibria in the Presence of Platinum

During previous studies (1-4), it was observed that mixtures of air with the same concentrations of SO_2 , H_2S , CH_3SH or COS produce identical emf's. This led to the conclusion that these gases were first converted into sulphur oxides. It was then determined that the following equilibrium is reached in the vicinity of the platinum electrode:



Thus, for a detector with a platinum electrode, the emf may be expressed in terms of PSO_2 in the sample by rewriting Equation 5:

$$E = \left[\frac{RT}{2F} \ln \frac{PSO_2 (PO_2)^{1/2}}{K_2} (PO_2)^{1/2} \right] + Ct \quad (7)$$

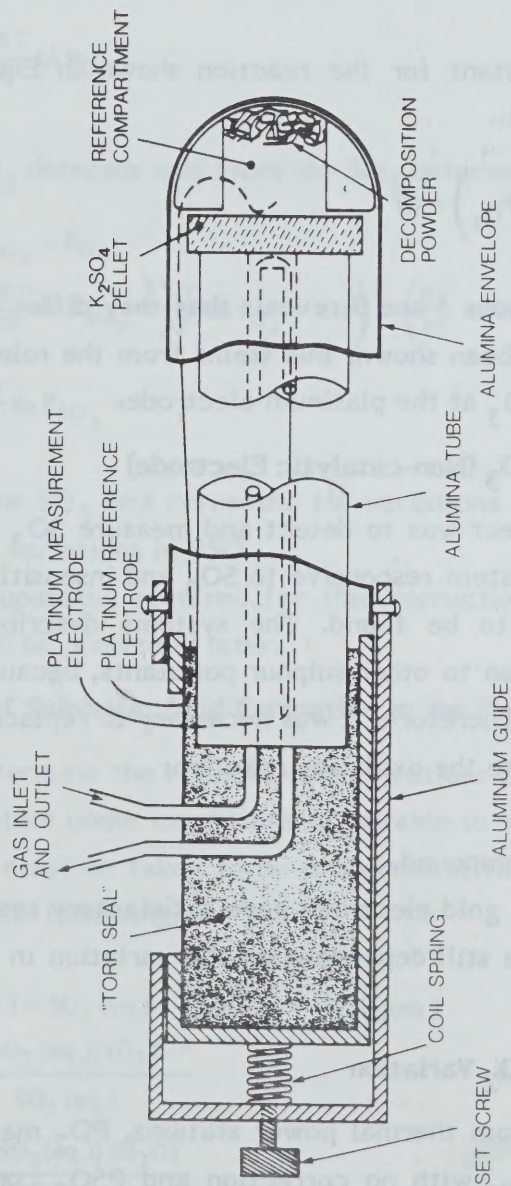


FIGURE 2 DESIGN OF A DETECTOR WITH A CLOSED REFERENCE CHAMBER WHERE DECOMPOSITION OF A POWDER MAINTAINS THE PARTIAL PRESSURE OF SO_3 , SO_2 AND O_2 CONSTANT

since:

$$P_{SO_3} = \frac{P_{SO_2} (P_{O_2})^{1/2}}{K_2} \quad (8)$$

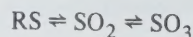
where K_2 is the equilibrium constant for the reaction shown in Equation 6. The emf accordingly is given by:

$$E = \left(\frac{RT}{2F} \ln P_{SO_2} \right) + \left(\frac{RT}{2F} \ln P_{O_2} \right) + C_t \quad (9)$$

A comparison of Equations 5 and 9 reveals that they differ only by a factor of two in the term " $\ln P_{O_2}$ ". As has been shown, this stems from the role of the $\frac{1}{2}O_2$ in the catalytic conversion of SO_2 into SO_3 at the platinum electrode.

2.3 Specific Detection of SO_3 (Non-catalytic Electrode)

The object of this project was to detect and measure SO_3 specifically in the presence of other pollutants. A system responsive to SO_3 and insensitive to the presence of other sulphur pollutants had to be found. The systems described above respond effectively not only to SO_3 but also to other sulphur pollutants, because of the catalytic effect of the platinum electrode. Therefore, it was necessary to replace this electrode by another type that would not promote the oxidation reaction:



where RS represents any sulphur compound.

As will be seen later, a gold electrode gave satisfactory results. However, the emf of a gold electrode detector is still dependent on the variation in the oxygen partial pressure in the sample.

2.4 Signal Correction for PO_2 Variation

In gaseous emissions from thermal power stations, PO_2 may vary from 0.05% to 5%. For this variation in PO_2 , with no correction and PSO_3 constant, the emf in Equation 5 would vary from 0 to 90 millivolts (mV).

As indicated in IREQ patents, this variation in PO_2 in a sample of gaseous emissions can be offset by diluting the sample in a volume of air at least 10 times greater. Under these conditions, the variation in PO_2 in the sample would then be negligible compared with the total PO_2 entering the sensor.

However, instead of resorting to a change in the sample a more sophisticated technique was adopted using an oxygen detector; this detector works on the same principle as the IREQ detector but has a zirconia electrolyte. The emf of a zirconia oxygen detector (6) of this type is given by:

$$E_{O_2} = \frac{RT}{4F} \ln P_{O_2} \quad (10)$$

Subtracting the O_2 detector emf from the SO_3 detector emf (Equation 5), gives:

$$E_c = E_{SO_3} - E_{O_2} \quad (11)$$

$$\text{or } E_c = \left(\frac{RT}{2F} \ln P_{SO_3} + \frac{RT}{4F} \ln P_{O_2} + C_{te} \right) - \left(\frac{RT}{4F} \ln P_{O_2} \right) \quad (12)$$

$$\text{or } E_c = \frac{RT}{2F} \ln P_{SO_3} + C_t \quad (13)$$

" E_c " represents the SO_3 emf corrected for variations of PO_2 in the sample, meaning that it represents only variations in PSO_3 .

The apparatus required for this correction as well as the pertinent experimental results will be presented later.

2.5 Role of Sulphuric Acid Formation in the Presence of Water

To determine the relative concentrations of SO_2 , SO_3 and H_2SO_4 that will be present in the system under conditions favourable to sulphuric acid formation, the amount of sulphuric acid must be taken to be proportional to the quantity of SO_2 introduced, in accordance with the following:

$$SO_2(\text{int.}) = SO_2(\text{eq.}) + SO_3(\text{eq.}) + H_2SO_4(\text{eq.}) \quad (14)$$

$$K_2 = \frac{[SO_2(\text{eq.})] (O_2)^{1/2}}{SO_3(\text{eq.})} \quad (8a)$$

$$K_p = \frac{[(SO_3(\text{eq.})) (H_2O)]}{H_2SO_4(\text{eq.})} \quad (15)$$

where: int. = amount introduced
and eq. = amount at equilibrium.

By substitution one obtains:

$$H_2SO_4(\text{eq.}) = \frac{[SO_2(\text{eq.})] (O_2)^{1/2} (H_2O)}{K_2 K_p} \quad (16)$$

$$\text{SO}_2 (\text{eq.}) = \frac{K_2 K_p [\text{SO}_2 (\text{int.})]}{K_p (\text{O}_2)^{1/2} + K_2 K_p + (\text{H}_2\text{O}) (\text{O}_2)^{1/2}} \quad (17)$$

$$\text{SO}_3 (\text{eq.}) = \frac{(\text{O}_2)^{1/2} (K_p) [\text{SO}_2 (\text{int.})]}{K_p (\text{O}_2)^{1/2} + K_2 K_p + (\text{H}_2\text{O}) (\text{O}_2)^{1/2}} \quad (18)$$

Using the latter three relations, the quantities of $(\text{H}_2\text{SO}_4)_{\text{eq.}}$, $(\text{SO}_2)_{\text{eq.}}$, and $(\text{SO}_3)_{\text{eq.}}$ present in the system when (H_2O) , $(\text{SO}_2)_{\text{int.}}$, K_2 , K_p and (O_2) are known can be calculated. The values of K_2 and K_p used for these calculations are taken respectively from studies by Wagman and Evans, as reported by Stern and Weise (7), and by Bodenstein and Katayama (8).

They are respectively:

$$\log_{10} K_2 = 8.987 - \frac{5590}{T} - 1.21572 \log_{10} T \quad (19)$$

$$\log_{10} K_p = -\frac{4998.9}{T} + 1.75 \log_{10} T - 0.00057 T + 3 \quad (20)$$

To avoid any H_2SO_4 condensation on the walls of the tubes, the latter are maintained at temperatures above the dew point of sulphuric acid, which is calculated following Verhoff and Banchero (9) by:

$$\frac{1}{[2.276 \times 10^{-3}] - [2.94 \times 10^{-5} \ln (\text{H}_2\text{O})] - [8.58 \times 10^{-5} \ln (\text{H}_2\text{SO}_4)] + [6.2 \times 10^{-6} \ln (\text{H}_2\text{O}) \ln (\text{H}_2\text{SO}_4)]} \quad (21)$$

3 EXPERIMENTAL

3.1 Preparation of Samples of SO_3 in Air

Two methods were considered for the preparation of SO_3 in air mixtures: a) injection of pure SO_3 into synthetic air; b) catalytic conversion of a known sample of SO_2 into SO_3 . For practical reasons the second method was selected. As previously described (1-4), a known concentration of SO_2 in dry air is prepared in a Mylar bag and then circulated through a catalytic converter consisting of a quartz tube with an enlargement containing alumina granules covered with platinum (Figure 3). During tests, the platinum catalyst was raised to various temperatures and different concentrations of SO_2 in air circulated through it. Figure 4 shows that the desired mixtures of SO_2 , SO_3 and air were successfully prepared, with the results conforming closely to theoretical expectations.

The concentration of SO_2 in air, as well as the ratio of SO_2 to SO_3 in the mixture after passage through the converter, were determined by the standard West-Geake method adapted to the measurement of these particular compounds (ASTM ÉDS-55-S9).

3.2 Detector Assembly

The set-up adopted has already been described in detail (1-4). As mentioned previously, the sensor was a pellet of K_2SO_4 , and a homogeneous $\text{MgO}/\text{MgSO}_4 + 4\% \text{Fe}_2\text{O}_3$ powder was sealed in the reference chamber (Figure 5).

A platinum electrode was always used in the reference chamber, but quartz was substituted for alumina and metal in the body of the detector to ensure that the inner wall of the sample chamber would not contribute to catalytic conversion of the mixture and that the mixture at no time would come into contact with any metal part.

During the initial tests, both a gold and a platinum electrode were used in the sample chamber. Later, a detector with a gold electrode and another with a platinum electrode were assembled separately and placed in separate ovens. The gas flow path is illustrated in Figure 3. All tubes were made of quartz and heated to $\approx 250^\circ\text{C}$ to avoid condensation of H_2SO_4 .

The SO_2 /air mixture first flows through a distilled-water bubbler (if a humid sample is required) immersed in a bath maintained at a constant temperature. It then flows through the catalyst for conversion of SO_2 into SO_3 . The resulting mixture flows through the gold electrode detector and finally through the platinum electrode detector.

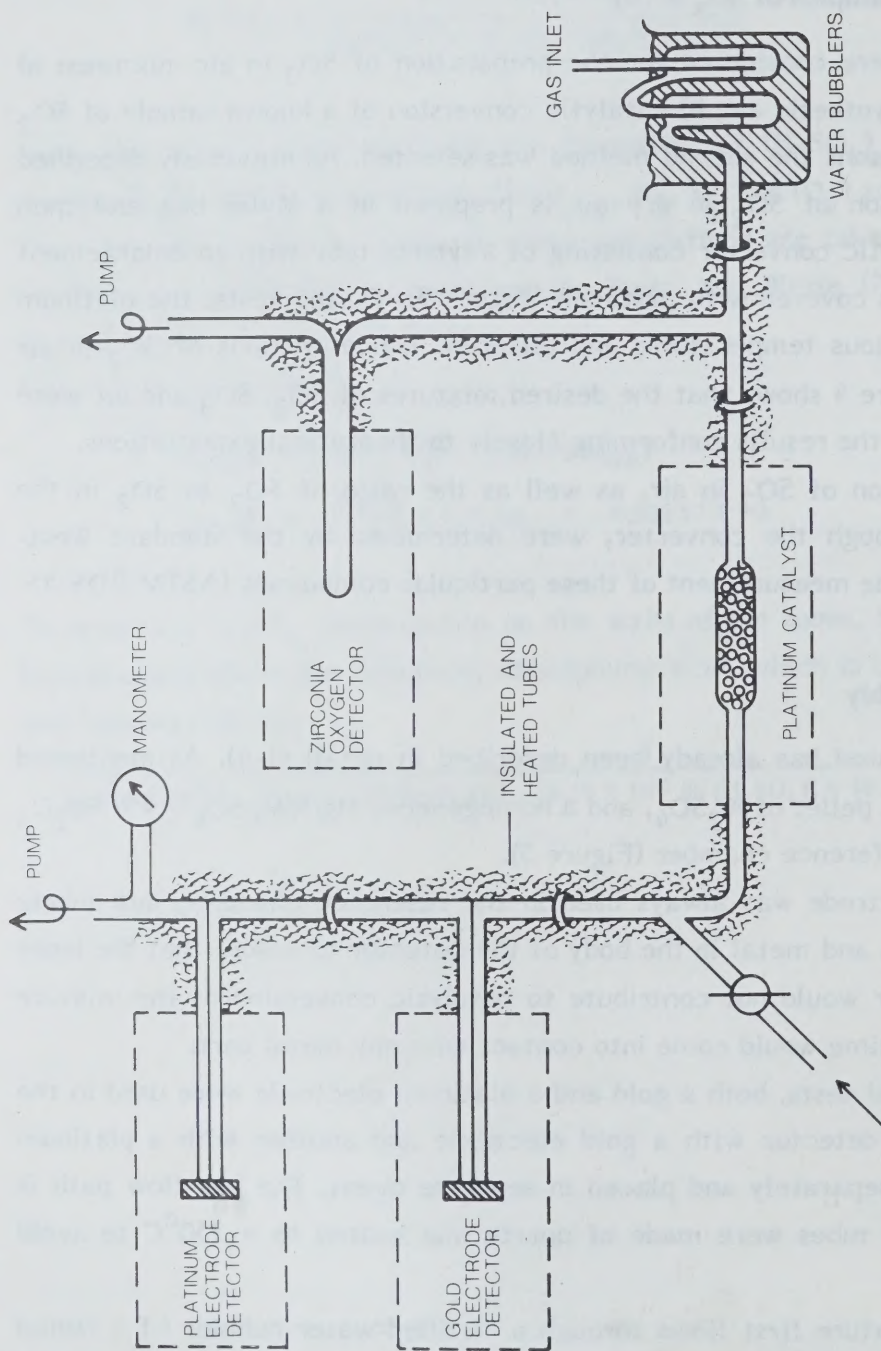


FIGURE 3 TEST ARRANGEMENT USED TO STUDY THE GOLD ELECTRODE DETECTOR'S SELECTIVITY IN MEASURING SO_3

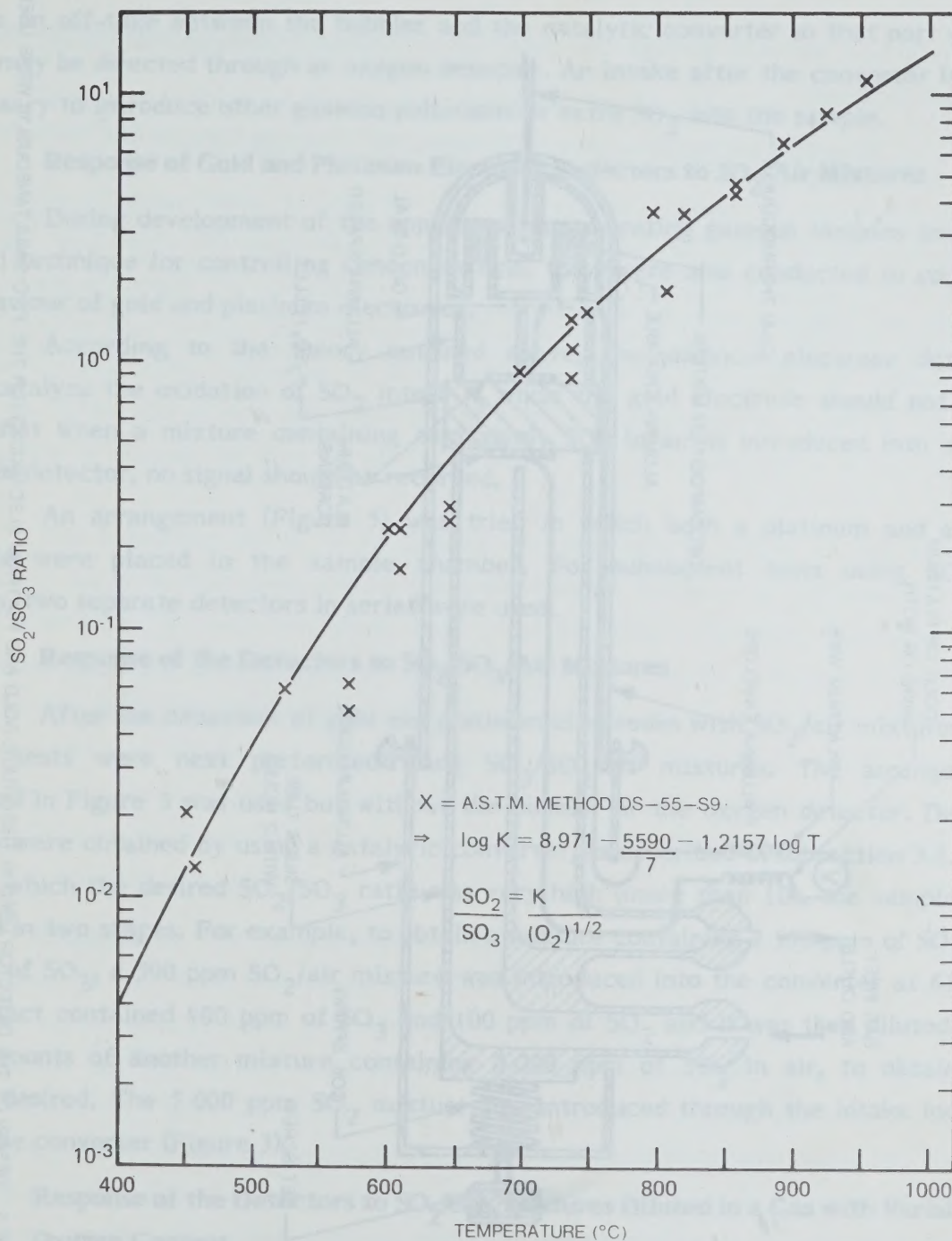


FIGURE 4 SO₂/SO₃ RATIO AS A FUNCTION OF THE TEMPERATURE OF THE CATALYST. THE THEORETICAL RELATION IS REPRESENTED BY THE SOLID LINE. THE EXPERIMENTAL RESULTS (X) WERE OBTAINED BY A.S.T.M. METHOD DS-55-S9.

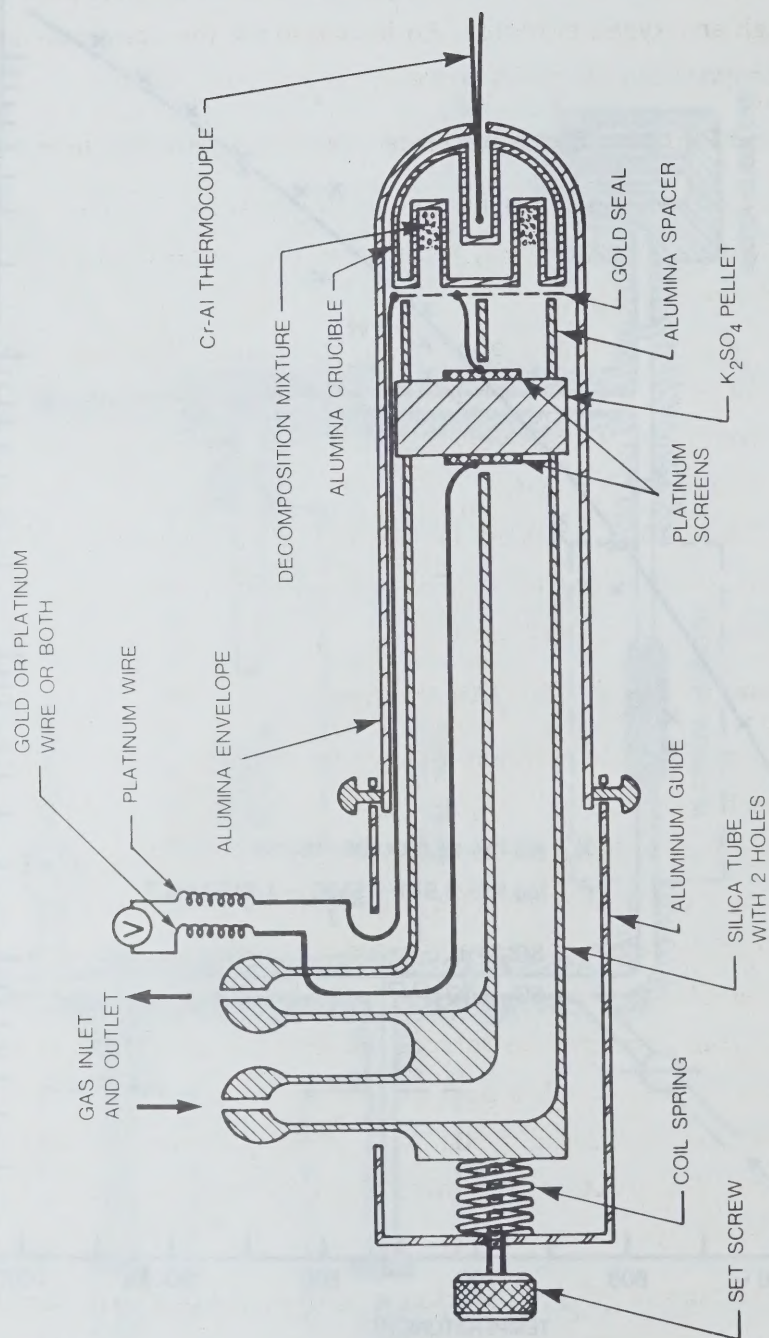


FIGURE 5 DESIGN OF THE DETECTOR USED IN THIS STUDY, GOLD AND PLATINUM ELECTRODES (OR THE TWO SIMULTANEOUSLY) WERE USED IN THE SAMPLE CHAMBER.

There is an off-take between the bubbler and the catalytic converter so that part of the sample may be directed through an oxygen detector. An intake after the converter is used if necessary to introduce other gaseous pollutants or extra SO_2 into the sample.

3.3 Response of Gold and Platinum Electrode Detectors to SO_2 /Air Mixtures

During development of the apparatus for generating gaseous samples and of a standard technique for controlling concentrations, tests were also conducted to compare the behaviour of gold and platinum electrodes.

According to the theory outlined above, the platinum electrode detector should catalyze the oxidation of SO_2 into SO_3 while the gold electrode should not. This means that when a mixture containing exclusively SO_2 in air is introduced into a gold electrode detector, no signal should be recorded.

An arrangement (Figure 5) was tried in which both a platinum and a gold electrode were placed in the sample chamber. For subsequent tests using SO_2 /air mixtures, two separate detectors in series were used.

3.4 Response of the Detectors to SO_2/SO_3 /Air Mixtures

After the behaviour of gold and platinum electrodes with SO_2 /air mixtures was studied, tests were next performed using SO_3/SO_2 /air mixtures. The arrangement illustrated in Figure 3 was used but without the bubbler or the oxygen detector. Desired mixtures were obtained by using a catalytic converter, as described in subsection 3.1. For cases in which the desired SO_2/SO_3 ratio was very high (more than 10), the sample was prepared in two stages. For example, to obtain a mixture containing 2 550 ppm of SO_2 and 200 ppm of SO_3 , a 500 ppm SO_2 /air mixture was introduced into the converter at 610°C . The product contained 400 ppm of SO_3 and 100 ppm of SO_2 and it was then diluted with equal amounts of another mixture containing 5 000 ppm of SO_2 in air, to obtain the mixture desired. The 5 000 ppm SO_2 mixture was introduced through the intake located beyond the converter (Figure 3).

3.5 Response of the Detectors to SO_2/SO_3 Mixtures Diluted in a Gas with Variable Oxygen Content

The response of a platinum electrode detector to variations in the oxygen content of the diluting gas has been described in detail in previous publications (3,4). The same procedure was followed to examine the behaviour of the gold electrode detector except that part of the $\text{SO}_2/(\text{N}_2 + \text{O}_2)$ mixture was circulated through the oxygen detector

(Figure 3) and the rest through the catalytic converter before passage to the detectors mounted in series.

3.6 Response of the Detectors to Mixtures with Varying Oxygen and Water Vapour Content

For this part of the testing, the full set-up illustrated in Figure 3 was used. Mixtures with varying water content were prepared by circulating the SO_2/air mixture through the bubblers with the bath maintained at a constant temperature between 20°C and 80°C . Within this temperature range, the H_2O content of the gas mixture may vary from 0 to 50%.

4 RESULTS AND DISCUSSION

4.1 Response of the Gold Electrode Detector to SO_2 /Air Mixtures

4.1.1 Tests with both a Platinum and a Gold Electrode in the Sample Chamber. At the beginning of these tests, a detector with a gold and a platinum electrode on the sample side was used. The response of each of the two electrodes to various mixtures of SO_2 in air was recorded. The results are summarized in Figure 6. According to this graph, in a newly assembled system the gold electrode responds much like the platinum electrode to concentrations under 100 ppm of SO_2 , but the response levels off at higher concentrations. After the system has been in use a while, the catalytic action of the gold increases and is similar to that of platinum at up to 5 000 ppm after three days of operation.

This behaviour seems to be caused by the catalytic effect of the platinum right next to the gold electrode, and by the deposition of platinum or platinum oxide on the gold electrode. To test this, small tubes covered with a platinum dispersion were placed in the gas inlet tube. It was found, as anticipated, that the presence of platinum leads to an $\text{SO}_2 \rightleftharpoons \text{SO}_3$ equilibrium, and the gold electrode produces a signal identical to that of the platinum electrode. Also, X-ray fluorescence analysis revealed traces of platinum on the gold electrode. It was concluded that another arrangement should be used to prevent contact between the platinum and the sample before the latter comes into contact with the gold electrode.

4.1.2 Response of the Gold Electrode Detector to SO_2 /Air Mixtures at Varying Temperatures. In this test, two separate detectors were placed in series. The SO_2 /air sample was admitted first to the gold electrode detector and then flowed through a quartz tube (heated to 300°C) into the detector with the platinum electrode. The initial results are summarized in Figure 7, which shows that at 805°C the gold electrode detector behaved in a manner similar to the platinum detector at concentrations below 100 ppm of SO_2 . However, as the temperature of the gold detector was lowered, its response to SO_2 became much weaker. The maximum concentration corresponding to the strongest signals at 640°C was of the order of 0.2 ppm. In terms of the study's objective, such a response may be considered negligible.

From the curves on Figure 7 it would appear that at temperatures lower than 760°C little catalytic conversion of SO_2 into SO_3 takes place at the gold electrode: there is not even a signal corresponding to 10 ppm. And as will be seen later, the response time

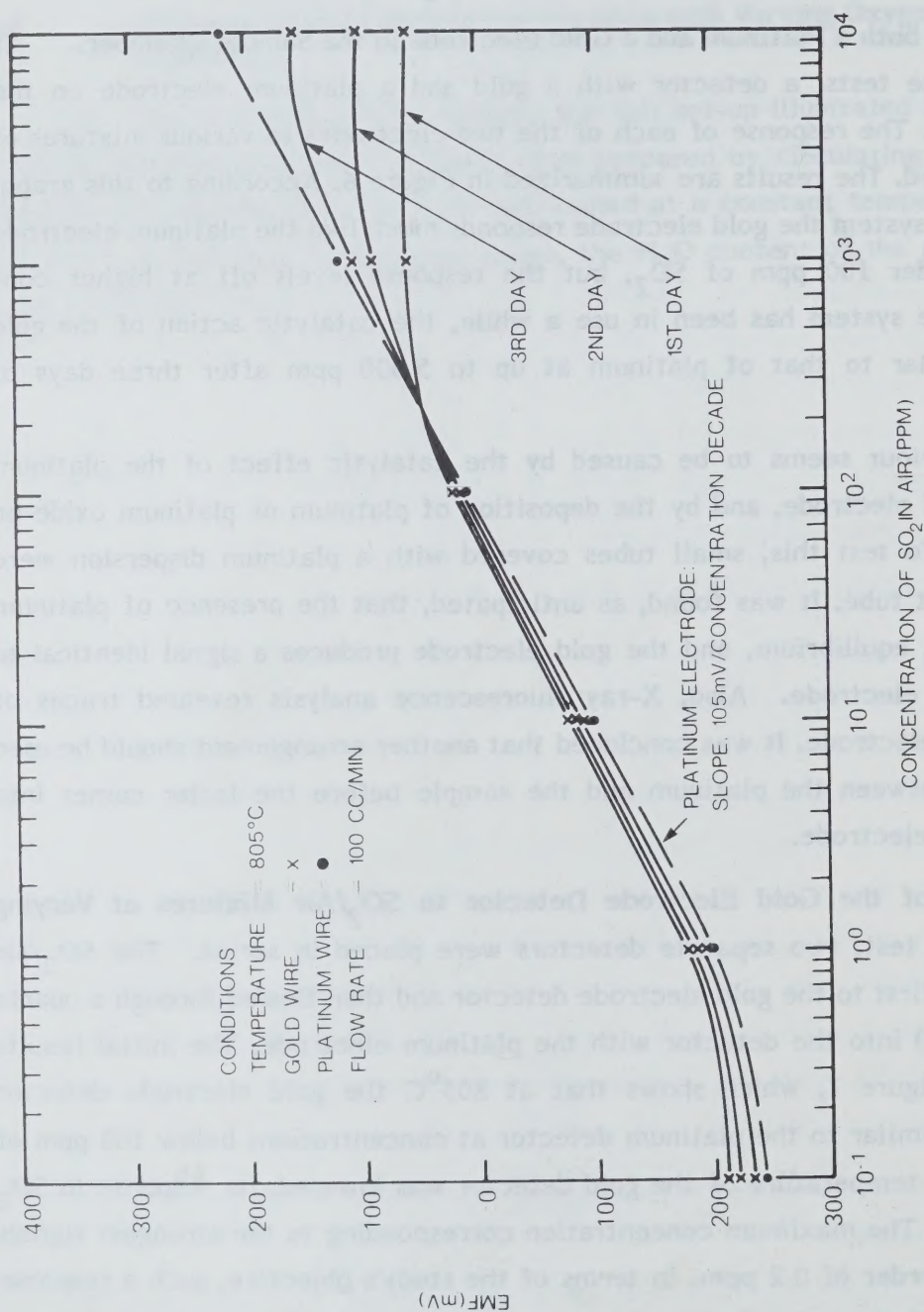
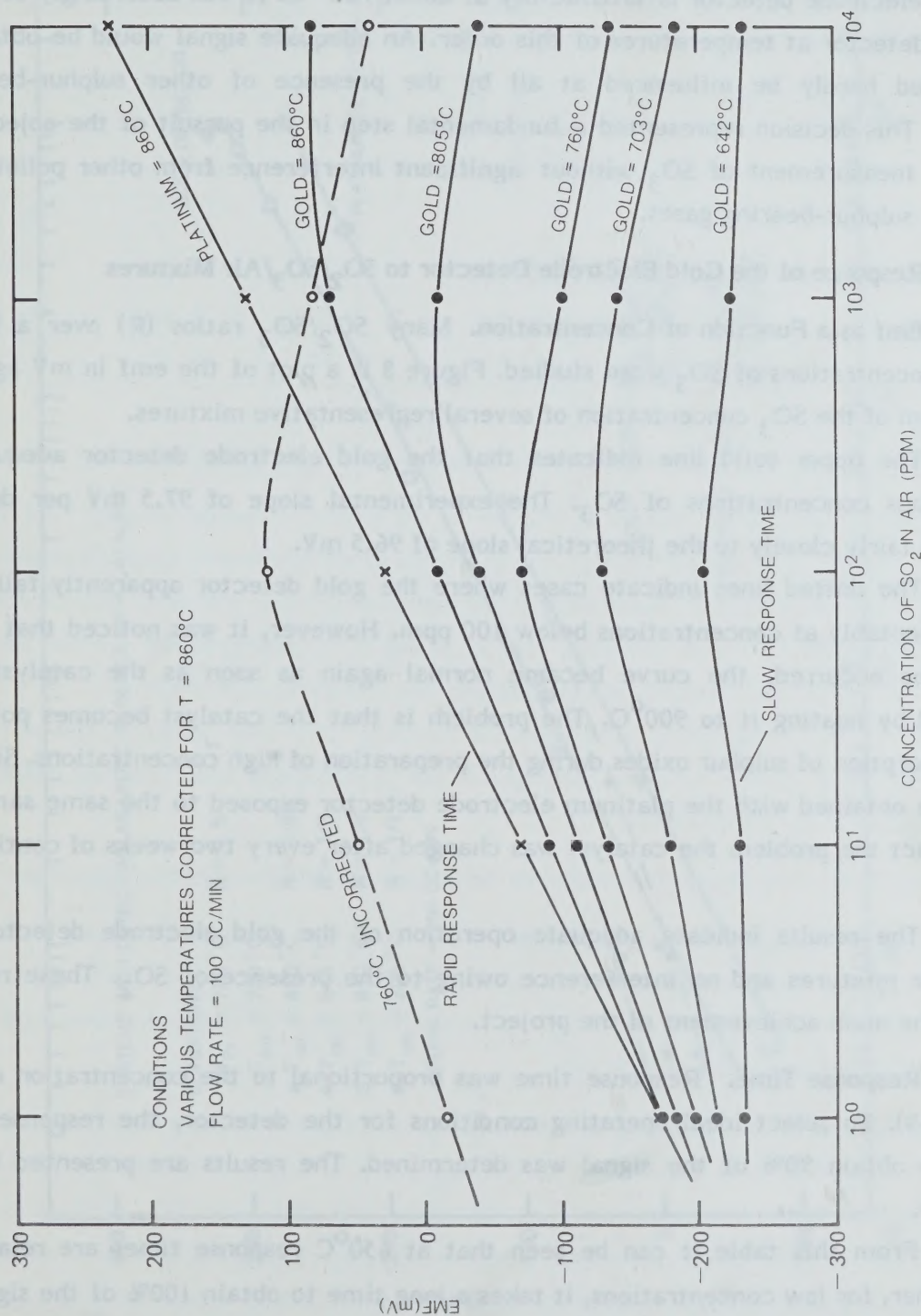


FIGURE 6 EMF AS A FUNCTION OF THE CONCENTRATION OF SO_2 IN AIR FOR A GAUGE WITH JUXTAPOSED GOLD AND PLATINUM ELECTRODES

FIGURE 7 EMF OF A GOLD ELECTRODE GAUGE, AT VARIOUS TEMPERATURES, AS A FUNCTION OF THE CONCENTRATION OF SO_2 IN AIR

of the gold electrode detector is satisfactory at about 700 °C. It was accordingly decided to use this detector at temperatures of this order. An adequate signal would be obtained and it would hardly be influenced at all by the presence of other sulphur-bearing pollutants. This decision represented a fundamental step in the pursuit of the objective, namely the measurement of SO₃ without significant interference from other pollutants, particularly sulphur-bearing gases.

4.2 Response of the Gold Electrode Detector to SO₂/SO₃/Air Mixtures

4.2.1 Emf as a Function of Concentration. Many SO₂/SO₃ ratios (R) over a broad range of concentrations of SO₃ were studied. Figure 8 is a plot of the emf in mV against the logarithm of the SO₃ concentration of several representative mixtures.

The upper solid line indicates that the gold electrode detector adequately senses various concentrations of SO₃. The experimental slope of 97.5 mV per decade corresponds fairly closely to the theoretical slope of 96.5 mV.

The dotted lines indicate cases where the gold detector apparently failed to operate acceptably at concentrations below 100 ppm. However, it was noticed that when such failures occurred, the curve became normal again as soon as the catalyst was regenerated by heating it to 900°C. The problem is that the catalyst becomes polluted through adsorption of sulphur oxides during the preparation of high concentrations. Similar curves were obtained with the platinum electrode detector exposed to the same samples. To counteract the problem the catalyst was changed after every two weeks of continuous operation.

The results indicate adequate operation of the gold electrode detector for SO₃/SO₂/air mixtures and no interference owing to the presence of SO₂. These results represent the main achievement of the project.

4.2.2 Response Time. Response time was proportional to the concentration of the mixture (1-4). To select ideal operating conditions for the detector, the response time required to obtain 90% of the signal was determined. The results are presented in the table below.

From this table it can be seen that at 650°C response times are relatively long. Further, for low concentrations, it takes a long time to obtain 100% of the signal -- over three minutes. From these findings, along with the earlier results regarding interference with measurement by SO₂, it was concluded that the ideal operating temperature for the detector should be between 700°C and 730°C.

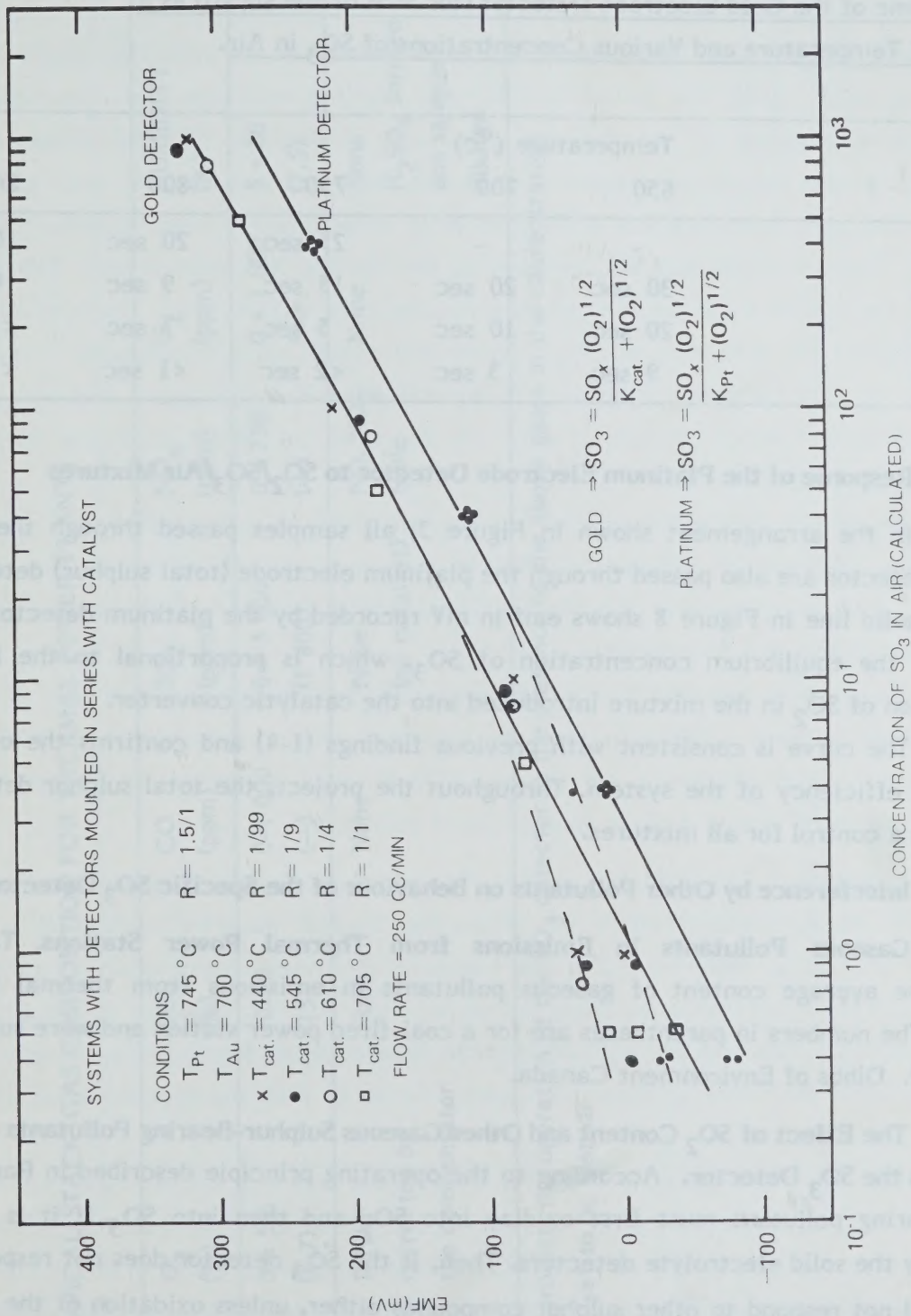


FIGURE 8 EMF OF A GOLD ELECTRODE DETECTOR AND PLATINUM ELECTRODE DETECTOR. FOR VARIOUS SO₂/SO₃ RATIOS. AS A FUNCTION OF THE EQUILIBRIUM CONCENTRATION OF SO₃ IN AIR

Response Time of the Gold Electrode Detector (for 90% of the signal) as a Function of Temperature and Various Concentrations of SO₃ in Air.

(SO ₃) (ppm)	Temperature (°C)				
	650	700	750	800	840
1	-	-	25 sec	20 sec	10 sec
10	30 sec	20 sec	15 sec	9 sec	4 sec
100	20 sec	10 sec	5 sec	3 sec	<1 sec
1 000	9 sec	3 sec	<2 sec	<1 sec	<1 sec

4.3 Response of the Platinum Electrode Detector to SO₂/SO₃/Air Mixtures

In the arrangement shown in Figure 3, all samples passed through the gold electrode detector are also passed through the platinum electrode (total sulphur) detector. The lower solid line in Figure 8 shows emf in mV recorded by the platinum detector as a function of the equilibrium concentration of SO₃, which is proportional to the initial concentration of SO₂ in the mixture introduced into the catalytic converter.

The curve is consistent with previous findings (1-4) and confirms the overall operational efficiency of the system. Throughout the project, the total sulphur detector was used as a control for all mixtures.

4.4 Interference by Other Pollutants on Behaviour of the Specific SO₃ Detector

4.4.1 Gaseous Pollutants in Emissions from Thermal Power Stations. Table 1 presents the average content of gaseous pollutants in emissions from thermal power stations. The numbers in parentheses are for a coal-fired power station and were supplied by Dr. H.P. Dibbs of Environment Canada.

4.4.2 The Effect of SO₂ Content and Other Gaseous Sulphur-Bearing Pollutants on the Signal from the SO₃ Detector. According to the operating principle described in Part 2, a sulphur-bearing pollutant must first oxidize into SO₂ and then into SO₃ if it is to be detected by the solid electrolyte detectors. Then, if the SO₃ detector does not respond to SO₂, it will not respond to other sulphur compounds either, unless oxidation of the latter produces SO₃ directly. Such an occurrence is most unlikely.

The tests described previously demonstrate that interference in the measurement of SO₃ created by low concentrations of SO₂ is negligible at temperatures below

TABLE 1 TYPICAL STACK-GAS COMPOSITION FOR THERMAL POWER PLANTS

Gas	O ₂ (%)	CO ₂ (%)	CO (ppm)	SO ₂ (ppm)	NO _x (ppm)	H ₂ (ppm)	HUMIDITY (%)	N ₂
Concentrations (coal)	0 → 5% (4.7)	10-20 (13)	0-1 000 (--)	0 → 5 000 (1 800)	0 → 750 (--)	0 → 1 000 (--)	5 → 20 (7.5)	Remainder (74.6)
Expected Influence	RT/4F corrected by the compensator	None	None	None (no catalyst)	NO, NO ₂ None	None	None H ₂ SO ₄ formed and sample diluted	

To complete the project, the operation of the SO₃ detector in the presence of the above gases in the concentration ranges shown has yet to be tested.

750°C (Figure 7). For tests with higher SO_2 concentrations, the assembly illustrated in Figure 3 was used. After the initial SO_2/SO_3 /air mixture was prepared, the extra SO_2 desired was introduced in the manner described in section 3.2 and schematically diagrammed at the bottom of Figure 9, in which findings from several such tests are presented. For each concentration of SO_3 , at least three different concentrations of SO_2 were tried. Table 2 shows the SO_2 content of the various mixtures tested. The line in Figure 9 is consistent with theoretical expectations (100 mV/decade). The scattering of points represents the influence of SO_2 content and is primarily attributable to residual catalysis at the gold electrode detector. As already observed in Figure 7, this is maximal at concentrations of about 100 ppm of SO_2 . In the cases considered here, the degree of scatter is acceptable (Table 2).

To ensure that other sulphur-bearing pollutants in no way distorted measurement of SO_3 , additions of 100 ppm of H_2S in air were made using the intake located beyond the catalytic converter. The results, presented in Figure 9, reveal that H_2S , like SO_2 , does not distort the SO_3 reading.

From these results, it may be concluded that the presence of SO_2 or other sulphur-bearing gaseous pollutants does not interfere with measurement of SO_3 by a detector with a gold electrode. Of course, efforts must be made to further reduce catalysis to the point where it plays no significant role at all.

4.4.3 Influence of CO_2 , CO , NO_x and H_2 , Separately or Together, on the Measurement of SO_3 . The experimental method for preparing SO_3 /air samples containing a fixed quantity of CO , CO_2 , NO_x or H_2 is the same as described previously. The lines in Figures 10 a, b and c represent the observed signal from the SO_3 detector in the presence of these pollutants. Their slopes are sufficiently close to those predicted by theory and it may be concluded that none of these pollutants interferes with the specific measurement of SO_3 .

Figure 11 is a graph of the emf obtained for two SO_3 concentrations (100 and 1 000 ppm) in mixtures containing all the gaseous pollutants found in stack emissions. The two observations represented by open circles confirm previous conclusions and exclude the possibility of synergistic effects interfering with the measurement. The solid line represents mixtures of SO_3 and SO_2 in synthetic air.

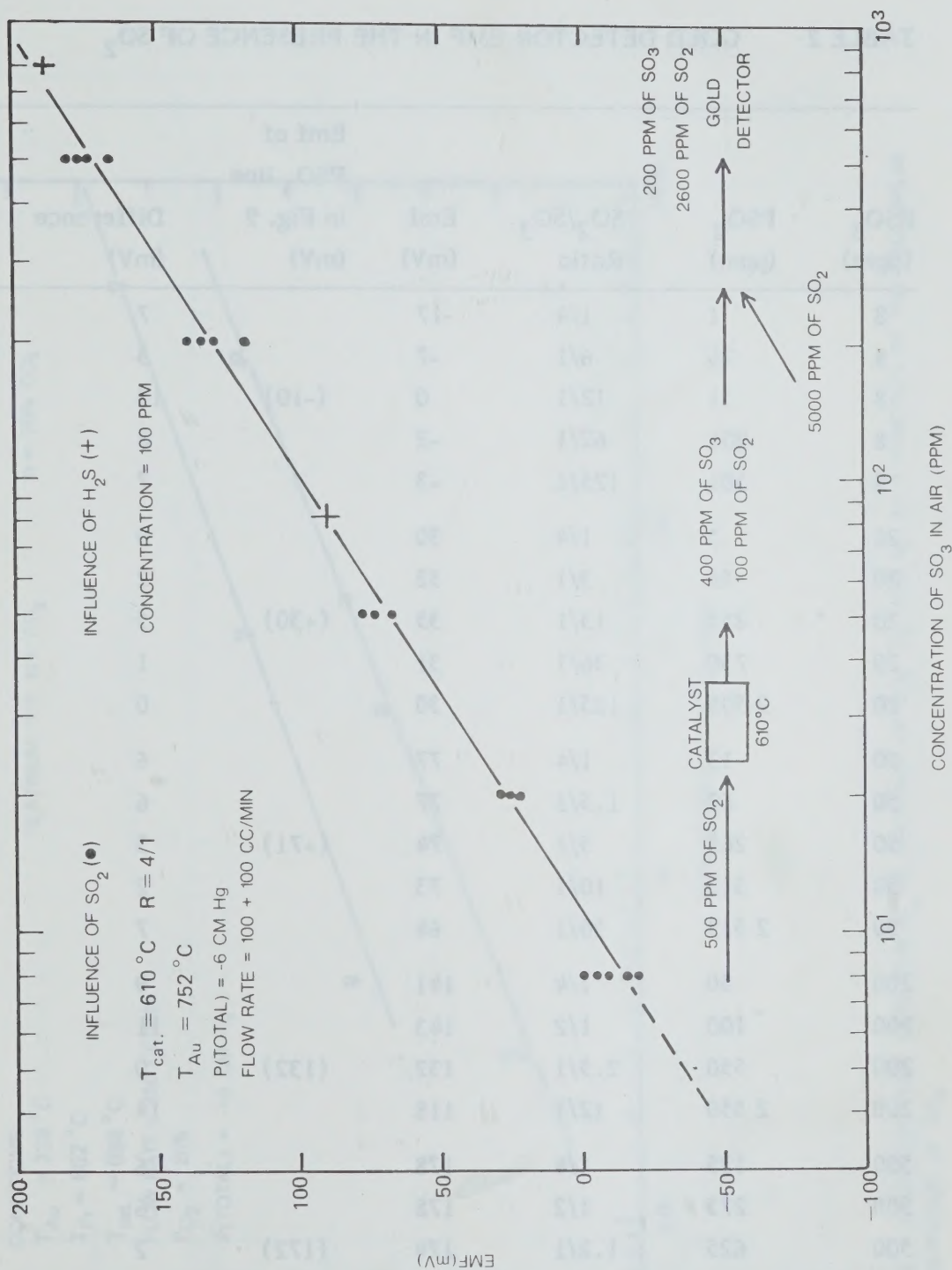


FIGURE 9 EMF AS A FUNCTION OF P_{SO_3} FOR A GOLD ELECTRODE DETECTOR IN THE PRESENCE OF OTHER SULPHUR COMPOUNDS (THE SO_2 CONTENTS ARE GIVEN IN TABLE 2; THE POINTS + SHOW THAT H_2S AT 100 PPM HAS NO EFFECT)

TABLE 2 GOLD DETECTOR EMF IN THE PRESENCE OF SO₂

PSO ₃ (ppm)	PSO ₂ (ppm)	SO ₂ /SO ₃ Ratio	Emf (mV)	Emf of PSO ₃ line in Fig. 9 (mV)	Difference (mV)	Maximum difference in percent of concentration*
8	1	1/4	-17		7	18
8	26	6/1	-7		3	10
8	51	12/1	0	(-10)	10	28
8	251	62/1	-2		8	20
8	501	125/1	-3		7	18
20	5	1/4	30		0	0
20	55	3/1	32		2	5
20	255	13/1	35	(+30)	5	12
20	730	36/1	31		1	2
20	2 505	125/1	30		0	0
50	13	1/4	77		6	15
50	63	1.5/1	77		6	15
50	263	5/1	74	(+71)	3	10
50	513	10/1	73		2	5
50	2 513	50/1	64		7	18
200	50	1/4	141		9	25
200	100	1/2	143		11	30
200	550	2.5/1	132	(132)	0	0
200	2 550	12/1	118		14	40
500	125	1/4	178		6	15
500	275	1/2	178		6	15
500	625	1.2/1	174	(172)	2	5
500	2 625	5/1	163		9	25

* Compared to the value measured on the line.

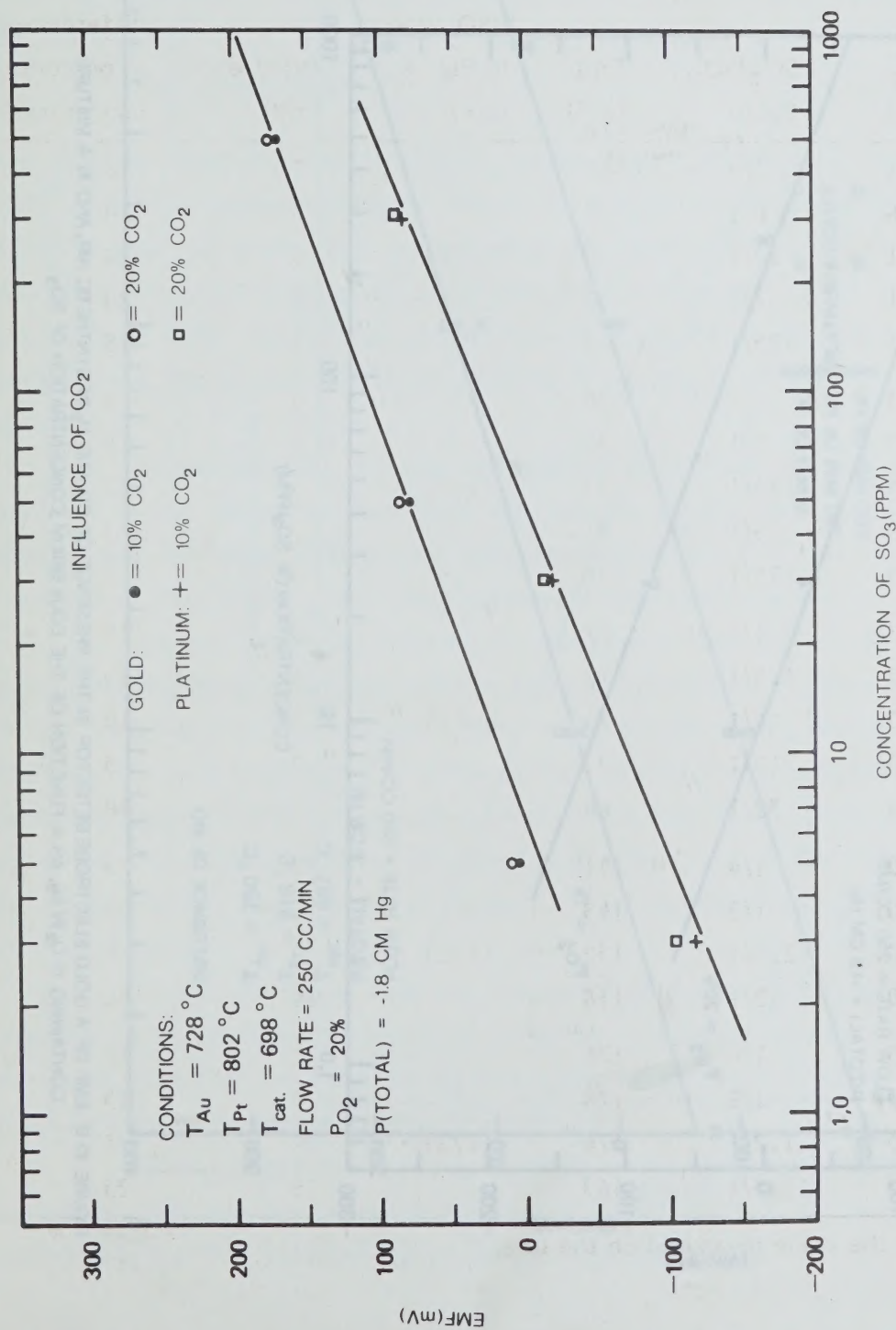


FIGURE 10A EMF OF A GOLD ELECTRODE DETECTOR IN THE PRESENCE OF CO₂, O₂, AND N₂, AS A FUNCTION OF THE EQUILIBRIUM CONCENTRATION OF SO₃

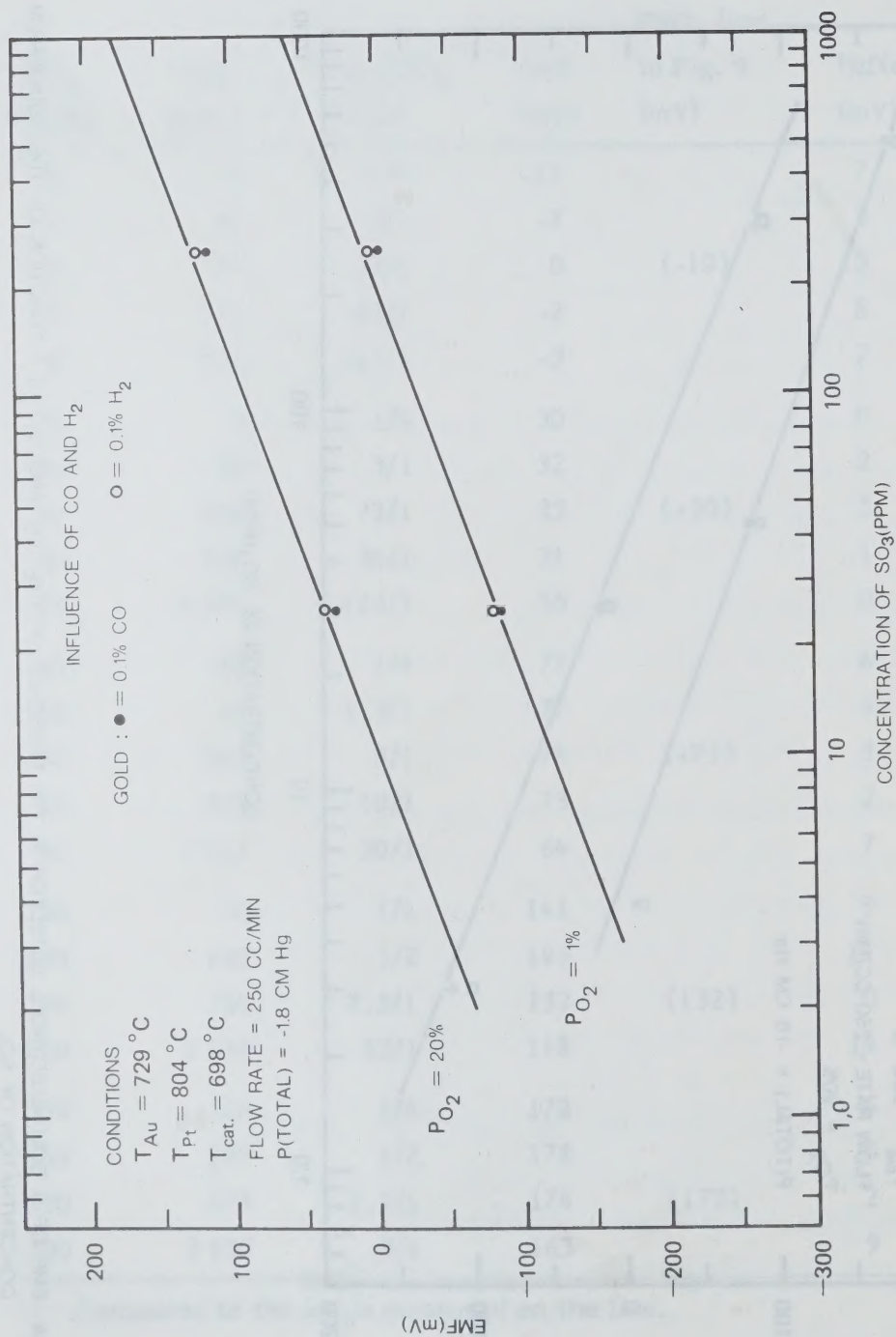
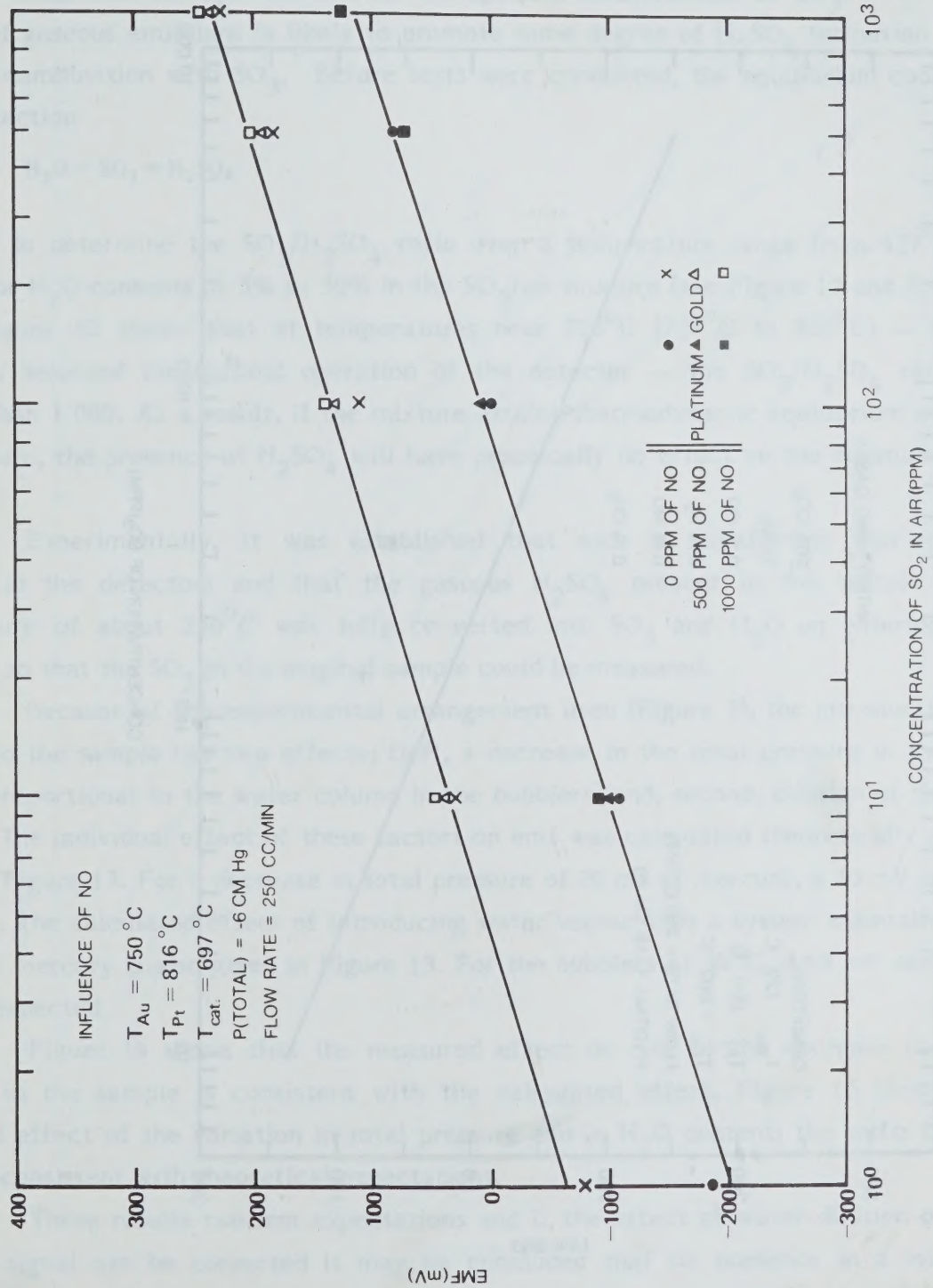


FIGURE 10 B EMF OF A GOLD ELECTRODE DETECTOR IN THE PRESENCE OF CO AND H₂ IN SYNTHETIC AIR, AND IN A MIXTURE CONTAINING 1% O₂ IN N₂, AS A FUNCTION OF THE EQUILIBRIUM CONCENTRATION OF SO₃

FIGURE 10C EMF OF A GOLD ELECTRODE DETECTOR IN THE PRESENCE OF NO, AS A FUNCTION OF THE CONCENTRATION OF SO_2 IN AIR

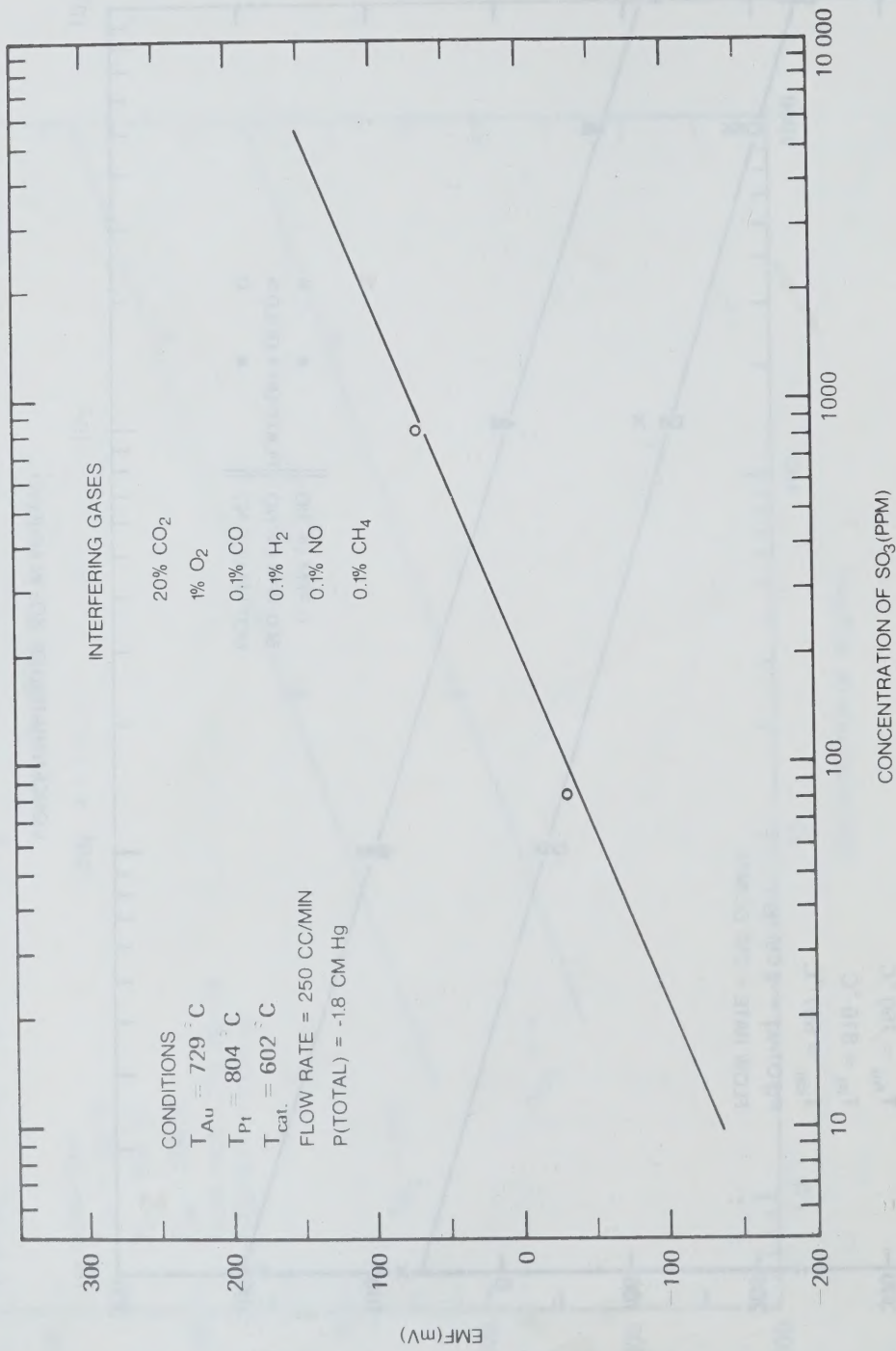
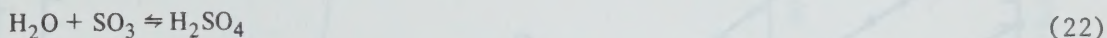


FIGURE 11 EMF OF A GOLD ELECTRODE DETECTOR IN THE PRESENCE OF H₂, CO, CO₂, NO, CH₄ AND SO₂ SIMULTANEOUSLY AS A FUNCTION OF THE EQUILIBRIUM CONCENTRATION OF SO₃ (THE FULL LINE IS A CALIBRATION CURVE IN SYNTHETIC AIR)

4.4.4 Influence of H₂O Content on the Specific Measurement of SO₃. The H₂O content of gaseous emissions is likely to promote some degree of H₂SO₄ formation as a result of combination with SO₃. Before tests were conducted, the equilibrium constant for the reaction



was used to determine the SO₃/H₂SO₄ ratio over a temperature range from 427°C to 1027°C for H₂O contents of 5% to 30% in the SO₃/air mixture (see Figure 12 and Section 2.5). Figure 12 shows that at temperatures near 725°C (727°C to 800°C) -- those previously selected for optimal operation of the detector -- the SO₃/H₂SO₄ ratio is greater than 1 000. As a result, if the mixture attains thermodynamic equilibrium at this temperature, the presence of H₂SO₄ will have practically no effect on the measurement of SO₃.

Experimentally, it was established that such an equilibrium was indeed attained in the detectors and that the gaseous H₂SO₄ present in the sample at a temperature of about 250°C was fully converted into SO₃ and H₂O on entering the detector, so that the SO₃ in the original sample could be measured.

Because of the experimental arrangement used (Figure 3), the introduction of water into the sample has two effects; first, a decrease in the total pressure in the gas circuit (proportional to the water column in the bubblers) and, second, dilution of the gas mixture. The individual effect of these factors on emf was calculated theoretically and is shown in Figure 13. For a decrease in total pressure of 20 cm of mercury, a 20 mV drop is expected. The calculated effect of introducing water vapour into a system maintained at 56 cm of mercury is also given in Figure 13. For the bubblers at 50°C, a 15 mV decrease is to be expected.

Figure 14 shows that the measured effect on emf of the decrease in total pressure in the sample is consistent with the calculated effect. Figure 15 shows the combined effect of the variation in total pressure and in H₂O content; the shifts of the lines are consistent with theoretical expectations.

These results confirm expectations and if the effect of water dilution on the detector signal can be corrected it may be concluded that its presence in a mixture analyzed by the SO₃ detector has no influence on the results.

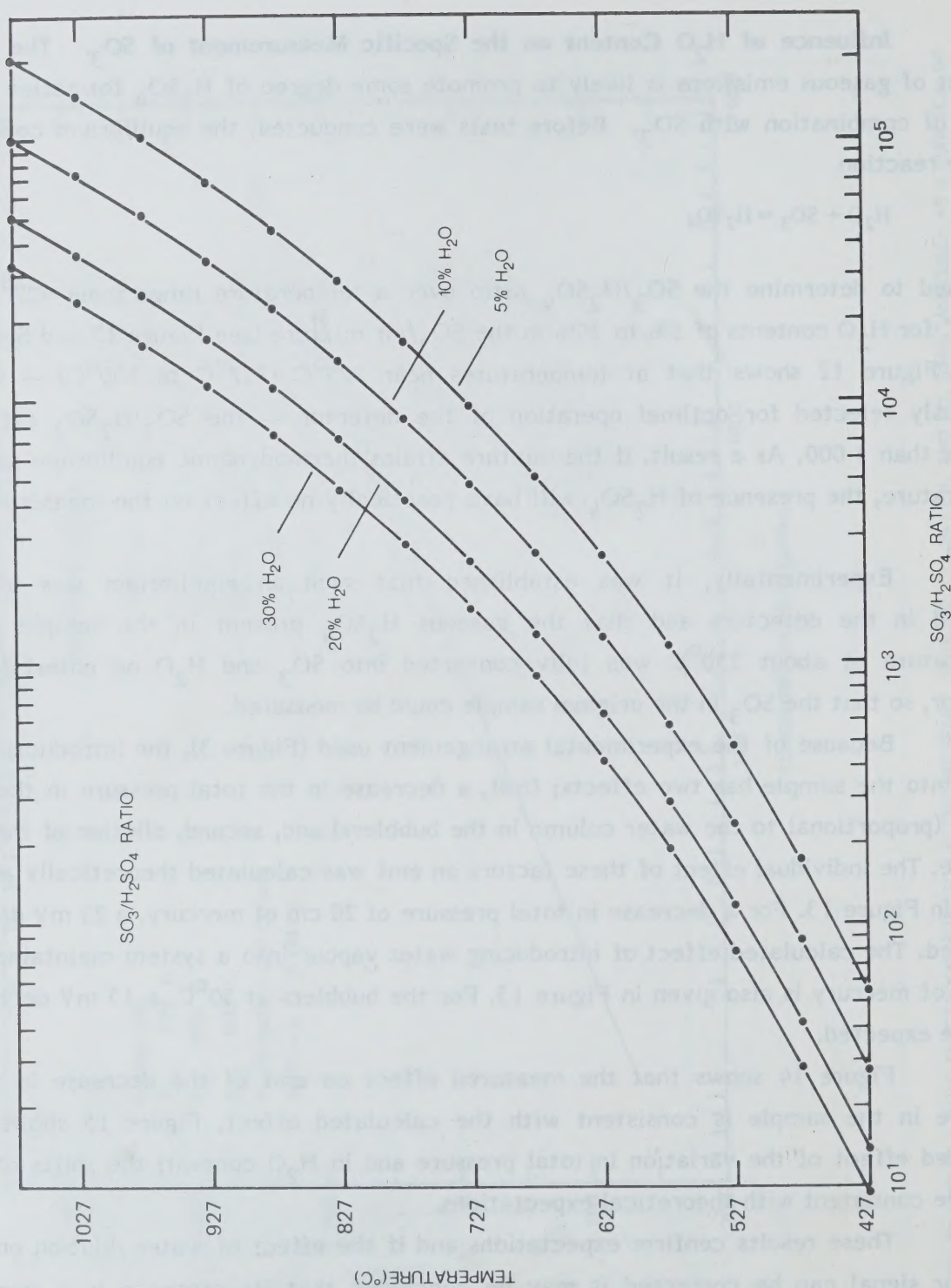


FIGURE 12 $\text{SO}_3/\text{H}_2\text{SO}_4$ RATIO AS A FUNCTION OF TEMPERATURE FOR VARIOUS CONCENTRATIONS OF WATER VAPOUR IN THE GAS

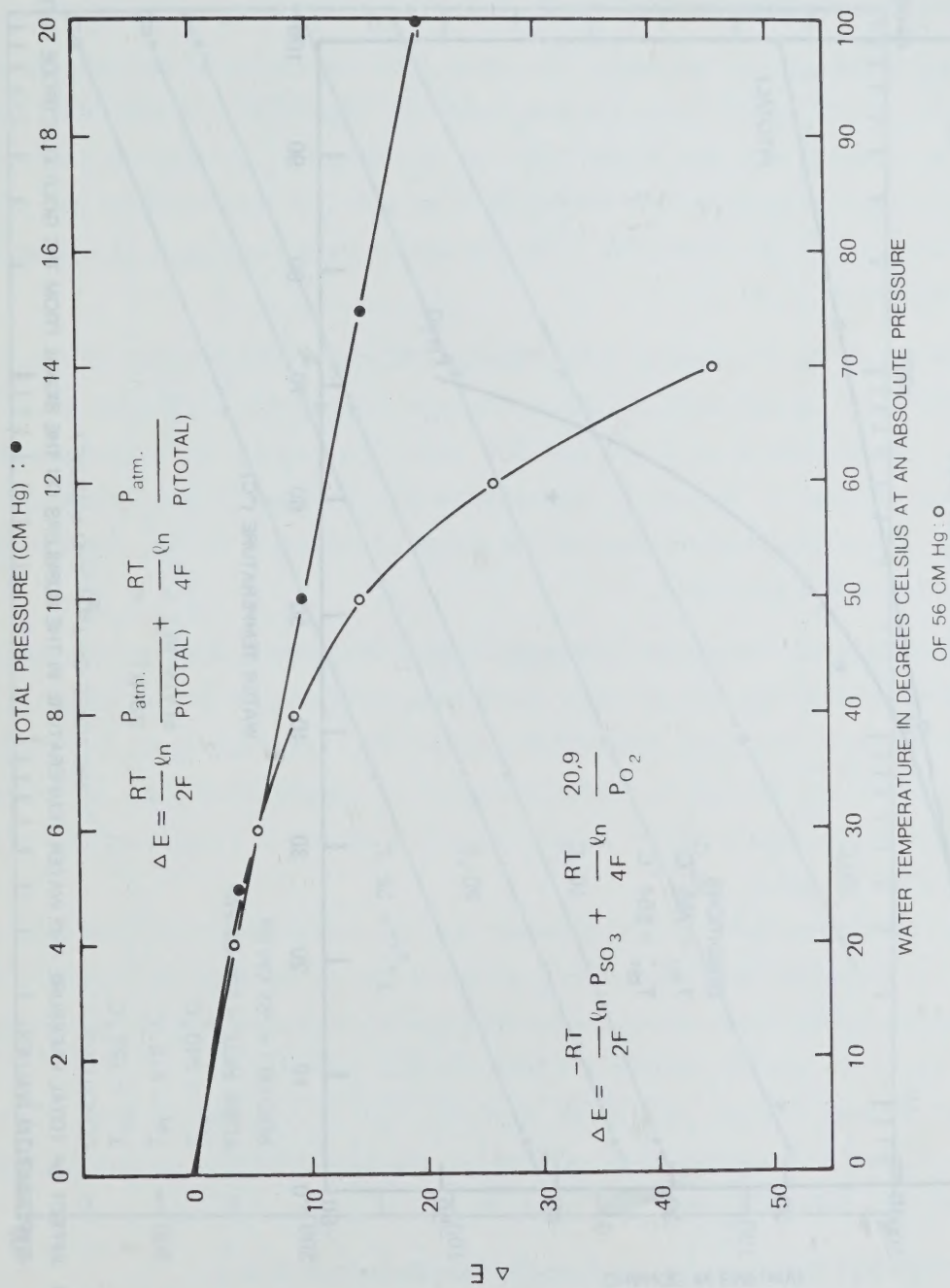


FIGURE 13 EFFECT OF TOTAL PRESSURE AND WATER TEMPERATURE IN THE BUBBLERS ON THE SIGNAL FROM THE GOLD ELECTRODE DETECTOR (CALCULATED VALUES)

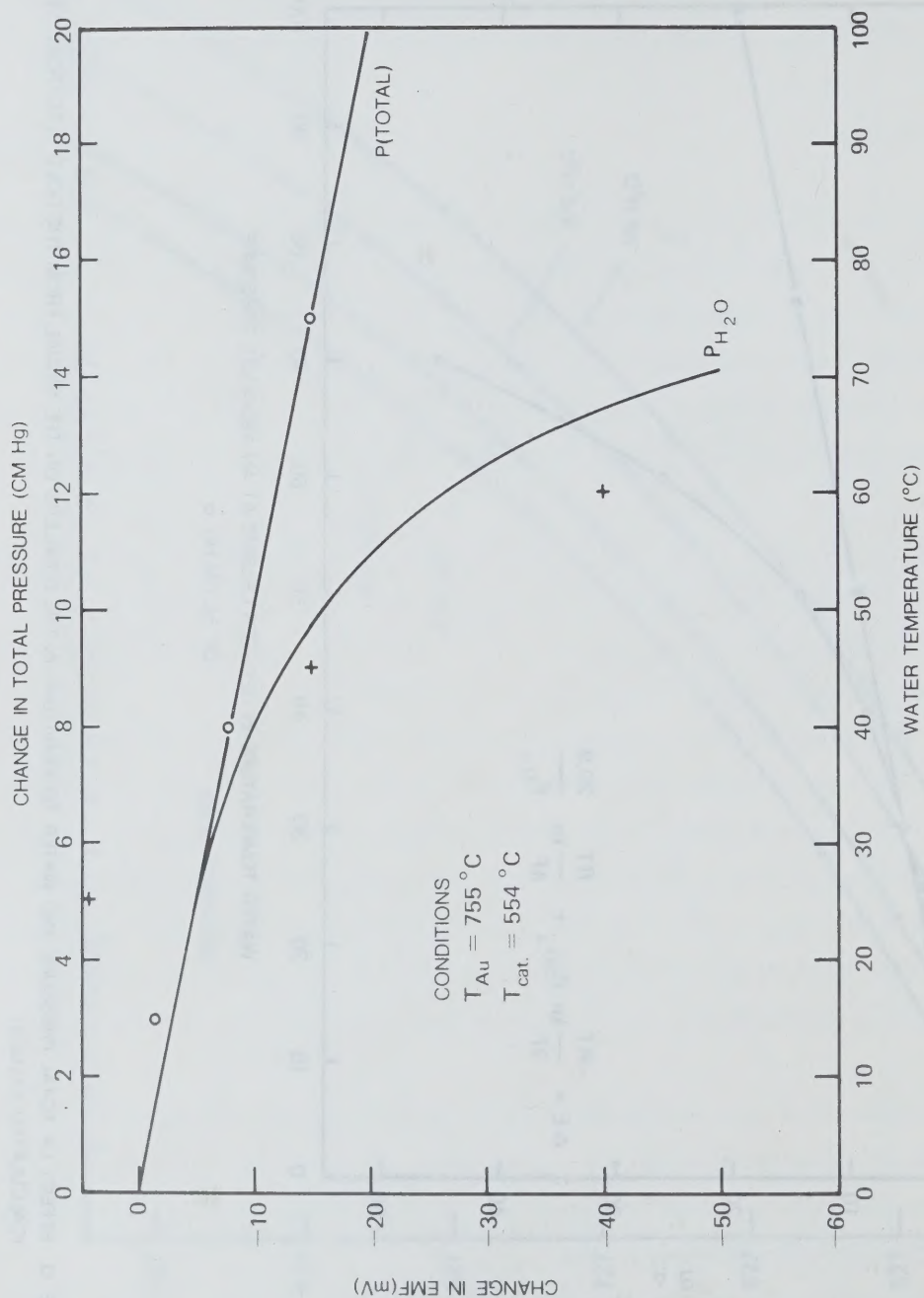


FIGURE 14 EFFECT OF TOTAL PRESSURE AND WATER TEMPERATURE IN THE BUBBLERS ON THE SIGNAL FROM THE GOLD ELECTRODE DETECTOR (EXPERIMENTAL VALUES)

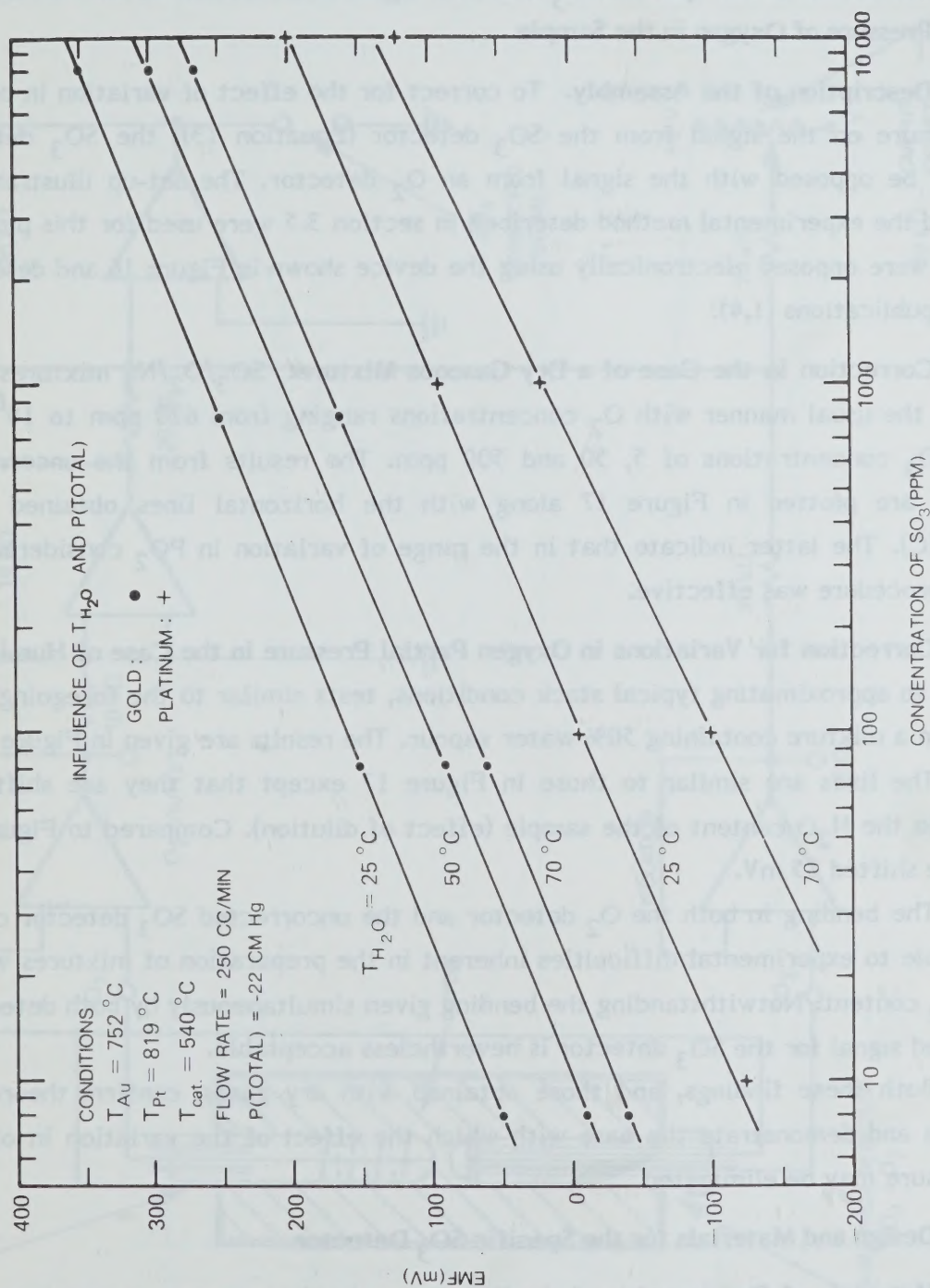


FIGURE 15 DISPLACEMENT OF THE EXPERIMENTAL CURVES BY THE COMBINED EFFECTS OF TOTAL PRESSURE AND WATER VAPOUR IN THE GAS

4.5 Correction of the Specific SO_3 Detector Signal as a Function of the Partial Pressure of Oxygen in the Sample

4.5.1 Description of the Assembly. To correct for the effect of variation in oxygen partial pressure on the signal from the SO_3 detector (Equation 13), the SO_3 detector signal must be opposed with the signal from an O_2 detector. The set-up illustrated in Figure 3 and the experimental method described in section 3.5 were used for this purpose. The signals were opposed electronically using the device shown in Figure 16 and described in previous publications (1,4).

4.5.2 Correction in the Case of a Dry Gaseous Mixture. $\text{SO}_3/\text{O}_2/\text{N}_2$ mixtures were prepared in the usual manner with O_2 concentrations ranging from 620 ppm to 10^6 ppm and with SO_3 concentrations of 5, 50 and 500 ppm. The results from the uncorrected signal (NC) are plotted in Figure 17 along with the horizontal lines obtained after correction (C). The latter indicate that in the range of variation in PO_2 considered, the correction procedure was effective.

4.5.3 Correction for Variations in Oxygen Partial Pressure in the Case of Humid Air. With a view to approximating typical stack conditions, tests similar to the foregoing were conducted on a mixture containing 50% water vapour. The results are given in Figure 18.

The lines are similar to those in Figure 17 except that they are shifted in proportion to the H_2O content of the sample (effect of dilution). Compared to Figure 17, the lines are shifted 85 mV.

The bending in both the O_2 detector and the uncorrected SO_3 detector curves is attributable to experimental difficulties inherent in the preparation of mixtures with a very low O_2 content. Notwithstanding the bending given simultaneously by both detectors, the corrected signal for the SO_3 detector is nevertheless acceptable.

Both these findings, and those obtained with dry gases, confirm theoretical expectations and demonstrate the ease with which the effect of the variation in oxygen partial pressure may be eliminated.

4.6 Design and Materials for the Specific SO_3 Detector

4.6.1 Materials of Construction of the Detector. At the very outset of the project, it was decided to use quartz instead of alumina and steel for the tubes with a view to preventing corrosion and minimizing adsorption and catalysis.

Tests were conducted to ensure that quartz and gold would not promote the catalytic conversion of the sample. The gas inlet tube was filled first with quartz chips

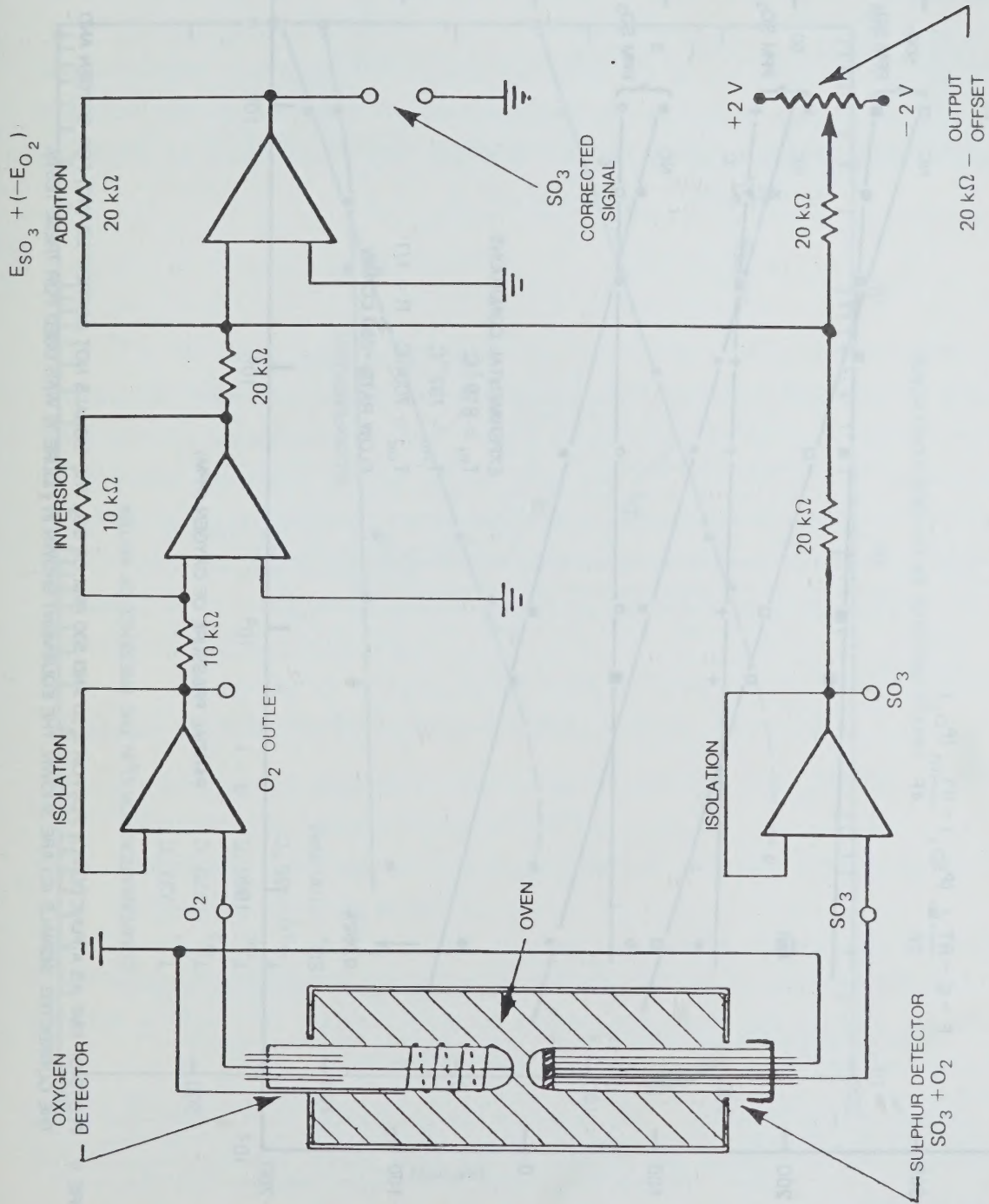


FIGURE 16. CIRCUIT DIAGRAM OF THE ELECTRONIC COMPENSATOR FOR ELIMINATING THE EFFECTS OF VARIATIONS IN OXYGEN PARTIAL PRESSURE ON THE GOLD ELECTRODE DETECTOR SIGNAL

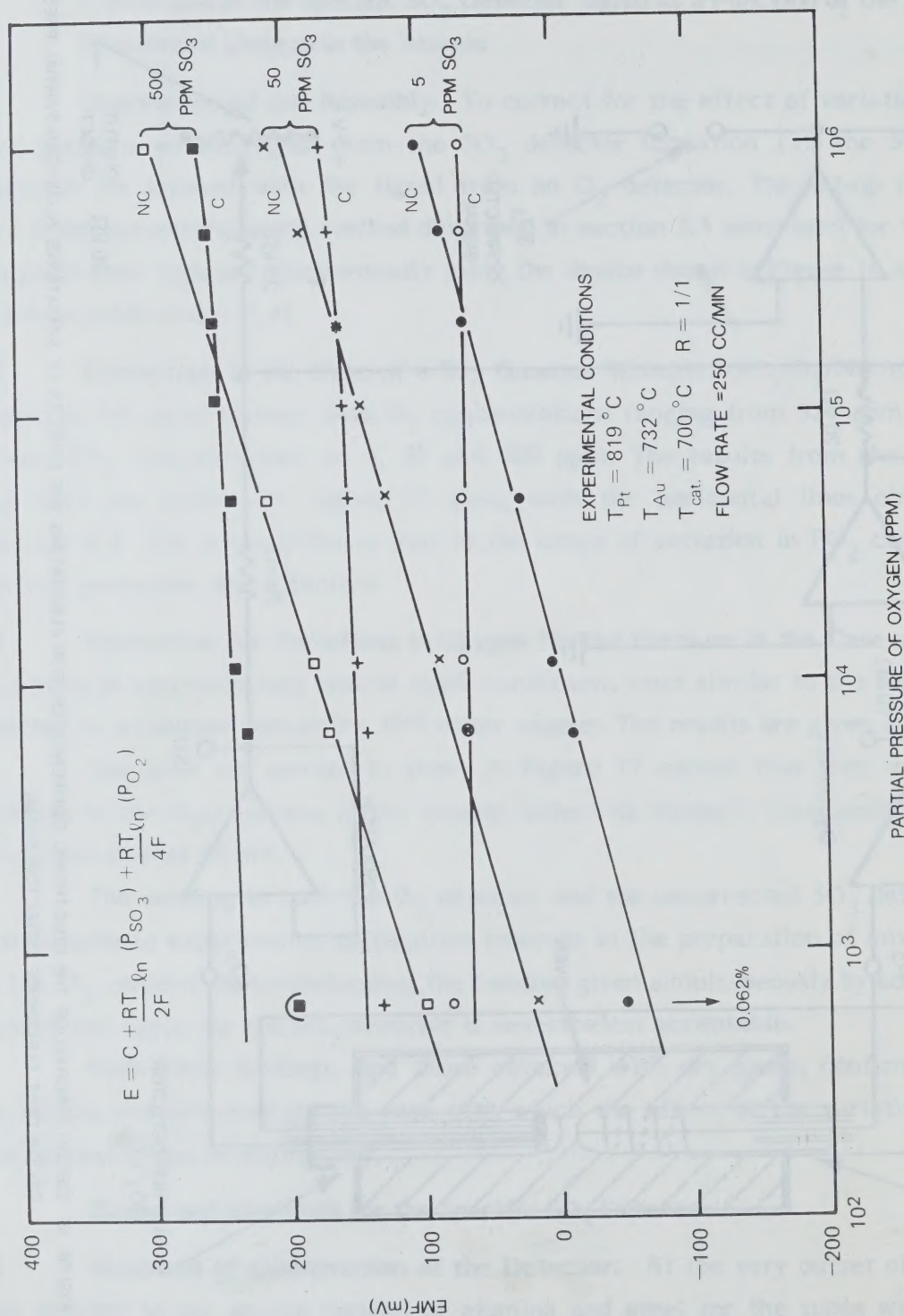


FIGURE 17 PLOTS OF EMF AS A FUNCTION OF PO_2 FOR 5, 50 AND 500 PPM OF SO_3 . THE SIGNALS NOT CORRECTED (NC) FOR OXYGEN AND THE CORRECTED SIGNALS (C) ARE SHOWN. THE EQUIPMENT SHOWN IN FIGURE 16 WAS USED FOR THESE TESTS.

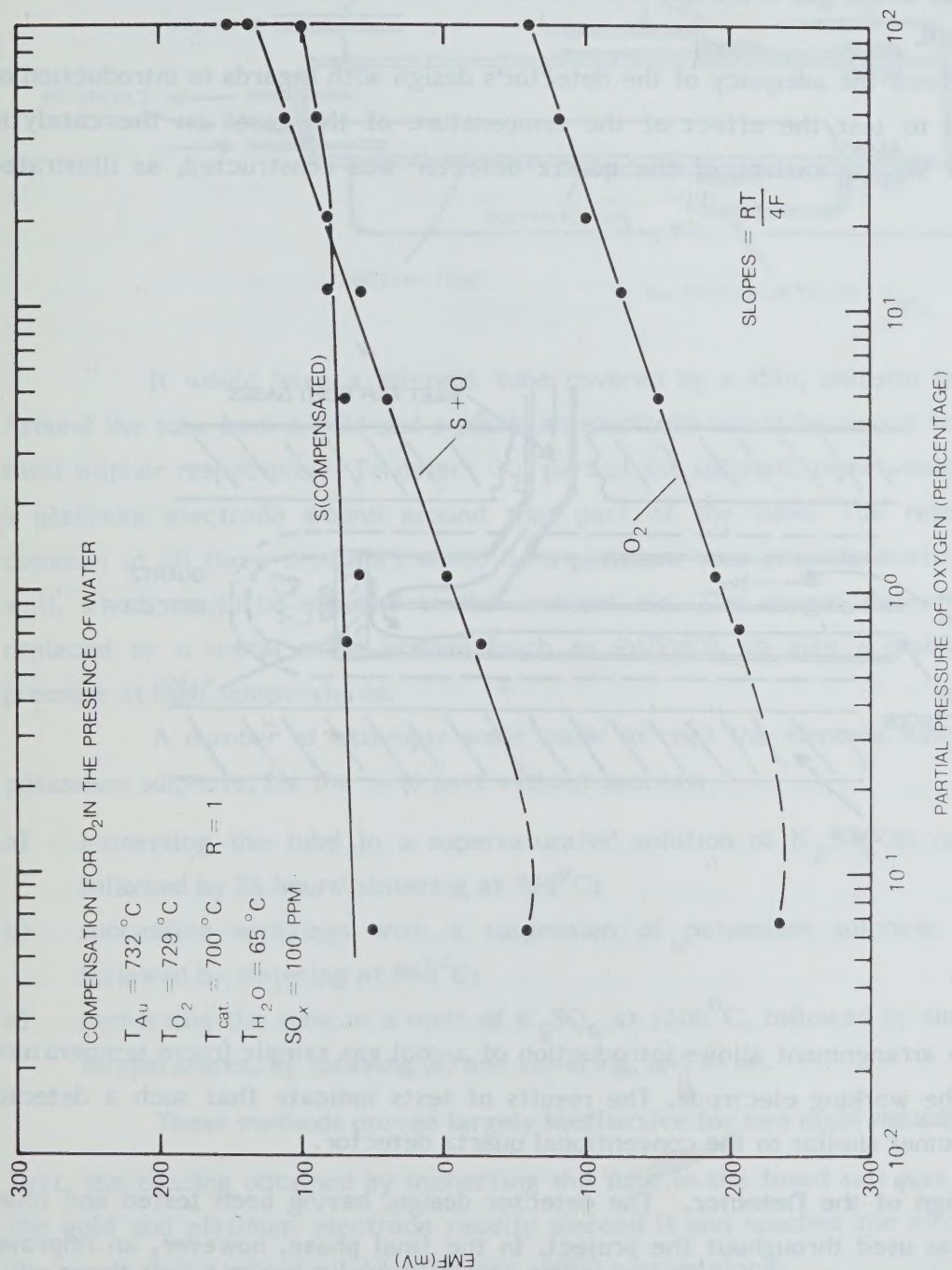
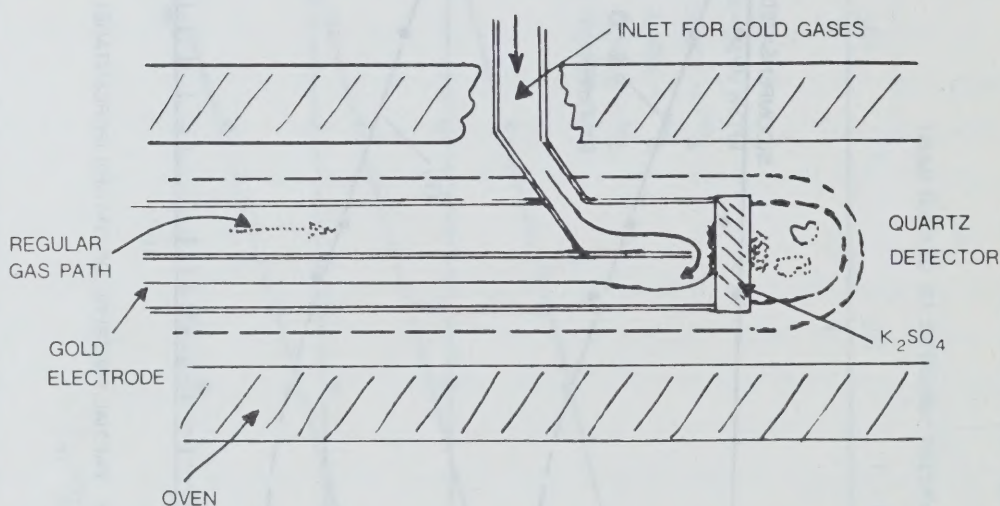


FIGURE 18 PLOTS OF EMF AS A FUNCTION OF P_{O_2} FOR 100 PPM SO_x IN A GAS CONTAINING 50% WATER VAPOUR (THE NON-COMPENSATED (S+O) AND COMPENSATED SIGNALS ARE SHOWN)

and then with gold filings or gold leaf. It was found that the detector having a large gold or quartz surface in the gas entrance tube behaved in an identical manner to one without the quartz or gold.

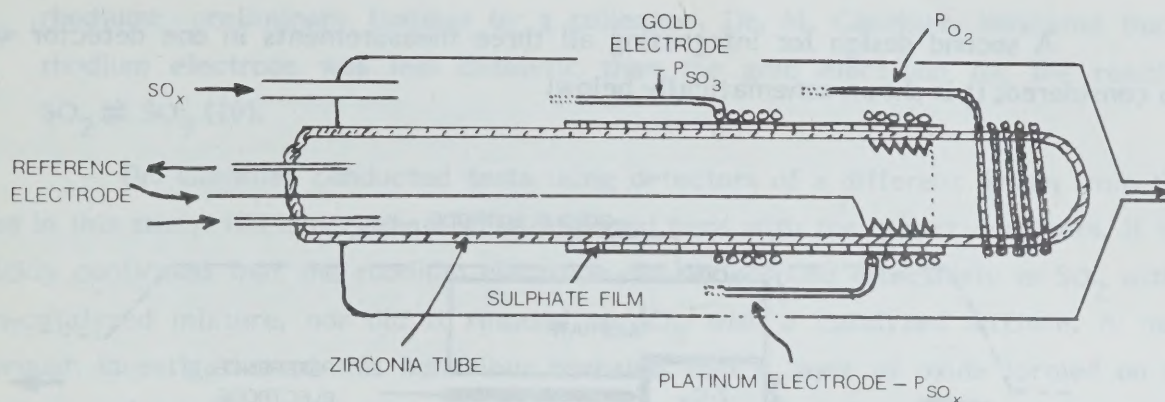
To check the adequacy of the detector's design with regards to introduction of the sample and to test the effect of the temperature of the gases on the catalytic reaction $\text{SO}_2 \rightarrow \text{SO}_3$, a variant of the quartz detector was constructed, as illustrated below:



This arrangement allows introduction of a cool gas sample (room temperature) directly onto the working electrode. The results of tests indicate that such a detector behaves in a manner similar to the conventional quartz detector.

4.6.2 Design of the Detector. The detector design, having been tested and found satisfactory, was used throughout the project. In the final phase, however, an improvement was attempted.

The objective was the simultaneous measurement of total gaseous sulphur, oxygen and sulphur trioxide in a single detector. Several systems were considered. The one felt to be best is illustrated below.



It would have a zirconia tube covered by a thin, uniform layer of sulphate. Around the tube both a gold and a platinum electrode would be wound to detect SO_3 and total sulphur respectively. To detect O_2 , part of the sulphate layer would be removed and a platinum electrode wound around that part of the tube. The reference electrode common to all three detectors would be a platinum wire in contact with the tube's inner wall, which would be exposed to the ambient air. The oxygen detector could also be replaced by a metal oxide system (such as Pd/PdO), to give a stable oxygen partial pressure at high temperatures.

A number of attempts were made to coat the zirconia tube with a layer of potassium sulphate, for the most part without success:

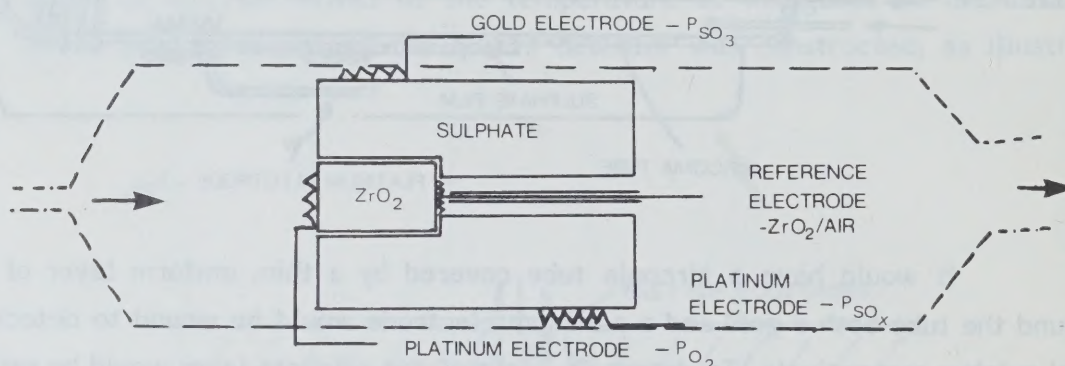
- immersing the tube in a supersaturated solution of K_2SO_4 at room temperature followed by 24 hours' sintering at 960°C ;
- successive sprayings with a suspension of potassium sulphate in hexane, also followed by sintering at 960°C ;
- immersing the tube in a melt of K_2SO_4 at 1100°C , followed by sintering at various temperatures, by spraying (b) and sintering, and so on.

These methods proved largely ineffective for two main reasons:

first, the coating obtained by immersing the tube in the fused salt was too thin, so that the gold and platinum electrode readily pierced it and touched the zirconia below, with the result that a mixed sulphate/oxygen signal was obtained;

second, the coating obtained by spraying was not sufficiently adhesive, meaning that it was extremely difficult to affix an electrode wire without destroying the coating. Further attempts should be made using other ways of applying the sulphate, other electrolytes and other sintering temperatures.

A second design for integrating all three measurements in one detector was also considered; it is shown schematically below.



Some technical limitations have prevented construction of such a detector, namely a mechanical property of the sulphate (resistance to drilling) and the different coefficients of thermal expansion.

It should be noted that it was technical problems and not the principle that prevented construction of a multi-purpose detector.

4.7 Selection of a Non-catalytic Electrode

According to the theory presented at the beginning of the report, for the specific measurement of SO_3 , oxidation of SO_2 to SO_3 must not be catalyzed by the detector's measurement electrode. Although results obtained with a gold electrode proved satisfactory, other electrode materials were tried. The choice is fairly restricted since the material must neither act as a catalyst nor react with the SO_2 at a high temperature. For example, silver could not be used because it would form silver sulphate.

The electrode materials tested were:

- a) gold amalgam: the gold electrode is placed in mercury and then heated to its operating temperature in the detector ($\approx 750^\circ\text{C}$) to stabilize the gold-mercury alloy at this temperature. The electrode is then used in a conventional detector. The few tests conducted using this system all showed that it was impossible to reduce the catalytic properties of gold by introducing mercury.

- b) rhodium: preliminary findings by a colleague, Dr. M. Gauthier, indicated that a rhodium electrode was less catalytic than the gold electrode for the reaction $\text{SO}_2 \rightleftharpoons \text{SO}_3$ (10).

Dr. Gauthier conducted tests using detectors of a different design from that used in this study. His experiments were repeated here with the quartz detectors. It was quickly confirmed that the rhodium electrode did not respond effectively to SO_2 with a non-catalyzed mixture, nor did it respond to SO_3 with a catalyzed mixture. A more thorough investigation of this behaviour revealed that a layer of oxide formed on the rhodium and totally changed its electrode properties. Dr. Gauthier used a platinum catalyst placed directly ahead of the rhodium wire in the gas inlet. It is highly likely that a small quantity of platinum was vapourized and deposited on the rhodium, giving it the properties of a catalytic electrode. Rhodium is thus not an adequate replacement for gold as a non-catalytic electrode.

1. Shaw, K.H. and J.L. Smith, *Technical Standard Reference Data*, International Union of Pure and Applied Chemistry, 1964.
2. Bodenstein, M. and M. Kaye, *Z. Elektrochem.*, 15, 364 (1911).
3. Verhoff, F.H. and J.E. Bowers, "Predicting Dew Point of Gas Gases", *Chem. Eng. Prog.*, 73, 71 (1973).
4. Gauthier, M., A. Belanger, A. Chamberland and B. Bouchard, "Progress in the Development of Solid Sulfate Sensors for Sulfur Oxides: Considering Gas Diffusion and Reference Electrodes", *Electrochem. Soc. Meeting Series*, Washington, May 1974.

5 CONCLUSION

The project goal has been achieved. A laboratory prototype of a specific SO_3 detector which operates adequately for gases similar to those contained in gaseous emissions from thermal power stations was developed.

The next logical step would be to develop an industrial prototype of a specific SO_3 detector and to devise a technique for constructing a multi-purpose detector.

This work should be done jointly by a Canadian manufacturer and IREQ, to ensure that the detector is marketed.

The results of the attempts to construct a multi-purpose detector indicate that more extensive research into the area of materials is necessary. Such research could well be considered the object of a subsequent project.

In the general field of measurement of pollutants and toxic gases using solid electrolyte detectors, IREQ could, under the present program, undertake further research projects on the measurement of the following gases: NO_2 , AsH_3 , PH_3 , SeH_2 , H_2S (in ambient air close to heavy water plants), carbon oxides and light hydrocarbons. Of these, H_2S around heavy water plants would seem to be of greatest concern, and a project leading to the design of a solid electrolyte detector (or alarm) for this pollutant could be undertaken.

BIBLIOGRAPHY

1. Chamberland, A., A. Bélanger and M. Gauthier, "Solid Electrolyte Detector for Sulfur-Bearing Pollutants Emitted by Industrial Stacks", 4th International Clean Air Congress - IUAPA, 1977, Tokyo, Japan.
2. Chamberland, A., and J.M. Gauthier, "Sensing Sulfur Oxides and Other Sulfur-Bearing Pollutants with Solid Electrolyte Pellets - 1. Gas Concentration Cells", *Atmos. Environ.* 11, 3, 257 (1977).
3. Gauthier, M., and A. Chamberland, "Solid State Detectors for Potentiometric Determination of Gaseous Oxides - 1. Measurement in Air", *J. Electrochem. Soc.* 124, 1579 (1977).
4. Gauthier, J.M., A. Chamberland, A. Bélanger and M. Poirier, "Solid State Detector for the Potentiometric Determination of Gaseous Oxides - 2. Measurements in Oxygen - Variable Gases in the SO_2 , SO_3 , O_2 , Pt/SO_4 = System", *J. Electrochem. Soc.* 124, 1584 (1977).
5. A. Chamberland and M. Gauthier, "Dispositif à l'état solide pour la détection de gaz polluants, Canada, Pat. 1,002,599 (1976)." Patents filed: U.S. 718,511; U.K. 23,561; Japan 50-1-949, 1978; Germany P. 25,56,483; Canada 234,645; France 75-12717 (obtained).
6. Ruka, R.J. and J. Weissbart, U.S. Pat. 3,400,054 (1968).
7. Stern, K.H. and E.L. Weise, National Standard Reference Data Series, Part 1, Sulfates, National Bureau of Standards 7, October 1966.
8. Bodenstein, M. and M. Katayama, *Z. Electrochem.* 15, 244 (1919).
9. Verhoff, F.H. and J.T. Banchemo, "Predicting Dew Point of Flue Gases", *Chem. Eng. Prog.*, 70, 71 (1974).
10. Gauthier, M., A. Bélanger, A. Chamberland and R. Bellemare, "Progress in the Development of Solid Sulfate Sensors for Sulfur Oxide: Circulating Gas Devices and Reference Electrodes", *Electrochem. Soc. Meeting*, Seattle, Washington, May 1978.

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